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PHYSICAL SCIENCES

Volume 9



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# PHYSICAL SCIENCES

Volume 9

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EDITED BY

SIR WILLIAM LAWRENCE BRAGG,  
C.H., O.B.E., M.C., F.R.S., M.A. (Cantab)

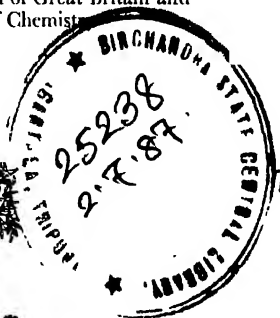
Professor Emeritus and formerly Director of the  
Royal Institution of Great Britain and Fullerian Professor of Chemistry

AND

PROFESSOR GEORGE PORTER,  
F.R.S., M.A., Sc.D. (Cantab)

Director of the Royal Institution of Great Britain and  
Fullerian Professor of Chemistry

REFERENCE



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Friday, February 1, 1924.

HIS GRACE THE DUKE OF NORTHUMBERLAND, C.B.E. M.V.O.,  
President, in the Chair.

SIR WILLIAM BRAGG, K.B.E. D.Sc. F.R.S. M.R.I.,  
Fullerian Professor of Chemistry.

### Recent Research on Crystalline Structure.

#### [ABSTRACT.]

THE more recent advances in the enquiry into the structure of materials which the discovery of the methods of X-ray analysis had rendered possible were dealt with. The extreme fineness of vision afforded by the X-rays had given a new insight into the way in which atoms were assembled into molecules, and the latter into all the immense variety of substances found in the earth, with all their diverse properties. Such new knowledge must give new light to all the sciences and to their application. Advances of vital importance were being made in many fields, and some of those that he and his fellow-workers were attempting to explore in the Davy Faraday Research Laboratory of the Royal Institution were described.

Of many striking consequences of the new work, one of the most remarkable was the way in which the chemist's vision of complex molecular structures had been verified. For example, the structure of benzene had been a great difficulty until Kekulé suggested that the six carbon atoms which it contained were arranged in the form of a ring—a suggestion which was the basis of half organic chemistry, and had led to the immense development of science with its dye-stuffs, explosives and other important substances. The X-ray methods had made it possible to measure the ring, and already to show how it was built into some of the simpler organic compounds. Similarly the long chains of carbon atoms which the chemist had imagined to be the basis of the molecular structure of a second great section of organic substances—oils, fats, and the like—had been shown by Piper, Shearer and Müller to be as they had been pictured. By a method due to Dr. Shearer and Dr. Müller, who were working in the Davy Faraday Laboratory, it was now possible to measure the exact dimensions of these chains; and some of the recent work was explained. Such work was of especial interest, because the long molecules had a habit of arranging themselves side by side on solid

and liquid surfaces, like oil on water, forming a sheet which profoundly affected the properties of the substance so cloaked; and this was a type of a number of important actions. Dr. Rideal, in the Cantor Lectures now being delivered before the Royal Society of Arts, had described how the groupings of molecules on a surface in this way sometimes led to a desired combination of the molecules, thus forced to rest side by side for a moment, and how the surface could be hindered from its proper effect, or "poisoned," by the spreading of a layer of the wrong substance. Actions of this kind were of fundamental importance in physiological processes and to some of our largest chemical industries.

The crystalline structure of metals, as revealed by X-rays, was another question which had been attacked by workers in different parts of the world. Metal-working had been carried on for ages by the human race, and had reached a pitch of development in which practice had far outrun theory. For instance, the use of tin to form an alloy with copper harder and more useful than the original material had brought in the Bronze Age long ago. Yet the explanation of the hardness of an alloy would only now seem to be forthcoming. It appeared that a pure metal like copper could be thought of as an assemblage of atoms which behaved like minute spheres, and were packed together as tightly as possible. When the copper was stretched or bent certain layers of these atoms slid over one another; and the sliding layers were those that were most densely packed with atoms, as one would perhaps expect. These layers formed planes of easy slip or weakness; and a single crystal of copper was very easily distorted because all the deformation was concentrated on the weak spots. When atoms of, for example, aluminium were introduced they took the place of some of the copper atoms, and, being larger, tend to lock the layers together and prevent the slip. Such was the explanation now being given by Rosenhain and his fellow-workers at the National Physical Laboratory as the result of an investigation by X-rays.

The hardening of metals like copper by cold-working was a very well-known effect, and this also was in process of being cleared up by X-ray analysts. The hardening had been shown to be accompanied by a re-arrangement of the crystals: this had been investigated especially in Germany, in connection with the operations of rolling and drawing. Some experiments made in the Davy Faraday Laboratory were described, which showed a simple effect of this kind to be the result of beating into foils. The X-rays revealed that the beaten leaves of gold, silver and copper and aluminium were formed of minute rectangular flaky crystals, one force being always parallel to the surface of the foil. When gold leaf was heated the flakes were disarranged and pointed in all directions. Faraday, and after him Sir George Beilby, had been greatly interested in these effects; and the new results were a further contribution to the knowledge of what

happened when a metal like copper was hardened by beating and softened again by annealing.

Reference was made to other researches now in progress at the Davy Faraday Laboratory, and of the part taken in promoting them by the workers there. The Davy Faraday Laboratory was an integral part of the Royal Institution, endowed by the late Ludwig Mond : containing a number of rooms fitted for chemical and physical research, and a very fine workshop ; benefiting also by its conjunction with the magnificent libraries of the Royal Institution. Nearly all the rooms were at present occupied, mainly by workers engaged on research by the X-ray methods, and many of these were financed by the Department of Scientific and Industrial Research. He believed that this work was of very great importance. It had been begun in England in the years immediately preceding the war, but in England at least had necessarily been laid aside until peace had restored the opportunities for its continuance. He trusted that the enthusiastic body of workers at the Davy Faraday Laboratory might be able, in conjunction with other workers in English laboratories, to make up the ground that had been lost to other countries, and to achieve results of benefit to pure science and to industry.

[W. H. B.]

Friday, February 8, 1924.

SIR ALFRED YARROW, BART, F.R.S. M.Inst.C.E.,  
Vice-President, in the Chair.

SIR WILLIAM BRAGG, K.B.E. D.Sc. F.R.S. M.R.I.,  
Fullerian Professor of Chemistry.

### The Scattering of X-Rays.

[ABSTRACT.]

THE scattering of X-rays is a peculiar effect which, X-rays being a form of light, has revived the old discussion as to the nature of light. The discussion began in earnest with Newton and Huyghens more than two hundred years ago. Newton believed in the existence of corpuscles of light which were emitted by the source of light and received by the eye. At the same time he believed in the existence of an ether in which waves could move, and he explained many of the light phenomena on the supposition that waves followed or accompanied the corpuscles and governed their motions. He rejected a pure wave theory on the ground that it was unable to explain the movement of light in straight lines, or in other words the casting of sharp shadows. We know now that this objection was faulty. Huyghens developed the pure wave theory, and in a masterly way showed how it could explain many of the phenomena which appeared during the passage of X-rays through crystals. He urged various objections to the corpuscular theory, as, for instance, that no material particles could possibly travel as fast as light, and again that rays of light could not pass through one another without mutual injury because the particles would collide. He was as unfortunate as Newton in his arguments against his opponent's theory.

During the nineteenth century there was a splendid development of the wave theory of light, which showed itself capable of explaining the most diverse phenomena in a satisfactory way. At the end of the century doubts began to creep in as to the ability of the now orthodox theory to explain all that radium and the X-rays had revealed; and the continuous rapid development of the new discoveries has turned the doubts into a certainty. Certain aspects of the new work can only be explained, to all appearances, on the ground that light travels in "quanta," which are in effect Newton's corpuscles. One of the most recent experiments seems to show, though the fact is

disputed, that the quantum of light may strike an electron and rebound therefrom as one billiard ball from another. It has recently been found at the Davy Faraday Laboratory that the experiment is as described, whatever the interpretation may be. There is an apparently irreconcilable difficulty as to the nature of light. How can it be both wave and corpuscle? It seems that Newton may be nearly right after all, in assuming that both descriptions are true, and that both wave and corpuscle are involved in the effects of light.

[W. H. B.]

Friday, April 4, 1924.

SIR JAMES CRICHTON-BROWNE, J.P. M.D. LL.D. D.Sc. F.R.S.,  
Treasurer and Vice-President, in the Chair.

SIR ERNEST RUTHERFORD, LL.D. D.Sc. F.R.S. M.R.I.,  
Professor of Natural Philosophy, R.I., and Cavendish Professor of  
Experimental Physics, University of Cambridge.

### The Nucleus of the Atom.

It is my intention this evening to give you an account of the present state of our knowledge of the atomic nucleus which controls the general structure of the outer atom, and thus its general physical and chemical properties. In a sense this minute but massive nucleus is a world of its own, which is little, if at all, influenced by the ordinary physical and chemical forces at our command. Time does not permit me to-night to deal with the other important side of the atomic problem—viz. the arrangement and motions of the outer or planetary electrons on which such a vigorous and successful attack has been made by Niels Bohr and his co-workers in recent years. In many respects the problem of nucleus structure is much more difficult than the corresponding problem of the planetary electrons, where we have a wealth of available information, both physical and chemical, to test the adequacy of our theories. The facts known about the nucleus are scanty in number, and the methods of attack to throw light on the nuclear structure are few and limited in scope.

There is now a general agreement that the atoms of all elements have a similar type of structure, consisting of a central positively charged nucleus of small dimensions surrounded at a distance by the appropriate number of electrons. From a study of the scattering of  $\alpha$  particles by the atoms of matter, and from the classical researches of Moseley on the X-ray spectra of the elements, we know that the resultant positive charge on the nucleus of any atom, in terms of the fundamental unit of charge, is given numerically by the atomic or ordinal number of the element, due allowance being made for certain missing elements. We know that with few exceptions all nuclear charges from 1 for the lightest atom hydrogen, to 92 for the heaviest element uranium, are represented by elements found in the earth. When we recall that the positions and motions of the planetary atoms are controlled mainly by the electrostatic forces from the nucleus, it is seen that the properties of an atom are

defined by a whole number which represents its nuclear charge, and only to a minor degree influenced by the atomic weight of the atom. It is convenient to distinguish sharply between the properties assigned to the nucleus and the planetary electrons. The movements of the electrons are responsible for the X-ray and optical spectra of the elements, and their configurations for the ordinary physical and chemical properties characteristic of the element. On the other hand, radioactive and all other properties that depend on the mass of the atom are to be definitely assigned to the nucleus.

A study of the long sequence of transformation in uranium and thorium, where either an  $\alpha$  particle, i.e. a charged helium nucleus, of mass 4, or a swift electron is ejected at high speed from the nucleus, shows that the nucleus contains not only positively charged bodies but also negative electrons, so that the positive charge on the nucleus represents the algebraic sum of the positive and negative charges contained in it. In recent years the general idea has arisen that there are two definite fundamental units that have to do with the building up of complex nuclei viz. the light negative electron and the relatively massive hydrogen nucleus which is believed to correspond to the positive electron. Such a view has received the strongest support from the important experiments of Aston on isotopes, in which he has shown that the masses of the various species of atoms are represented nearly by whole numbers in terms of  $O = 16$ . From general electric theory, it is to be anticipated that the mass of the hydrogen nucleus in the nucleus structure will be somewhat less than its value  $1.0077$  in the free state on account of the very close packing of the charged units in the concentrated nucleus. From Aston's experiments, it appears that the average mass of the hydrogen nucleus, or proton as it is now generally called, is very nearly  $1.000$  under these conditions. We should anticipate that the whole-number rule found by Aston would hold only to a first approximation, since the mass of the proton must be to some extent dependent on the detailed structure of the nucleus. In the case of tin and xenon Aston has already signalled a definite departure from the whole-number rule, and no doubt a still more accurate determination of the masses of the atoms will disclose other differences of a similar kind.

While our present evidence strongly indicates that the proton and electron are the fundamental constituents of the nucleus, it is very probable that secondary combining units play a prominent part in nuclear constitution. For example, the expulsion of helium nuclei from the radioactive bodies indicates that the helium nucleus of mass 4 is probably a secondary unit of great importance in atom building. On the views outlined we should expect the helium nucleus of charge 2 to be built up of four protons and two electrons. The loss of mass in forming this nucleus indicates that a large amount of energy must be liberated during its formation. If this

be the case, the helium nucleus must be such a stable structure that the combined energy of four or five of the swiftest  $\alpha$  particles would be necessary to effect its disruption. Such a deduction is supported by our failure to observe any evidence of disintegration of the swift  $\alpha$  particle itself, whether it is used to bombard matter, or whether the  $\alpha$  particle is used to bombard other helium atoms.

We shall now consider some of the lines of evidence which throw light on the question of the dimensions of the nucleus and the laws of force in its neighbourhood, the modes of vibration of the nucleus, and the effects observed when some nuclei are disintegrated by bombardment with  $\alpha$  particles.

### DIMENSIONS OF NUCLEI AND THE LAW OF FORCE.

The conception of the nucleus atom had its origin in 1911 in an attempt to explain the scattering of  $\alpha$  particles through large angles in passing through thin sheets of matter. The observation that the  $\alpha$  particle was deflected in some cases through more than a right angle as the result of an encounter with a single atom showed that very intense forces must exist within the atom, and these were ascribed to a minute but massive charged nucleus. It was shown by Geiger and Marsden that the number of  $\alpha$  particles scattered through different angles were in close accord with calculation based on the nuclear theory, when it was assumed that the electrostatic forces between the charged  $\alpha$  particle and the nucleus obeyed the ordinary law of the inverse square. The accuracy of this law has been independently verified, so that we are now fairly certain that in a region close to the nucleus the ordinary laws of force are valid.

These scattering experiments also gave us the first clue as to the probable dimensions of the nuclei of heavy atoms, for it is to be anticipated that the law of the inverse square must break down if the  $\alpha$  particle in a collision approaches closely to, or actually enters, the nuclear structure. This variation in the law of force would show itself by a difference between the observed and calculated numbers of particles scattered through different angles. Geiger and Marsden, however, found no certain variation even when the  $\alpha$  particles of range about 4 cms. were deflected through  $100^\circ$  by an encounter with a gold nucleus. In such an encounter the  $\alpha$  particle must approach to within about  $5 \times 10^{-12}$  cms. of the centre of the nucleus, so that it would appear that the radius of the gold nucleus, assumed spherical, could not be much greater than this value. When, however, we recall that the  $\alpha$  particle from a radioactive body has its origin in the nucleus and must increase in energy as it escapes through the repulsive field of the nucleus, calculation shows that in the case of a heavy element like uranium we should expect the law of force to begin to break down at a distance of about  $6 \times 10^{-12}$  cms. from the nuclear centre.



Our present information indicates that the nucleus of a heavy atom must have a radius of about  $6 \times 10^{-12}$  cms. It would, however, be of great interest to repeat the scattering of  $\alpha$  particles for angles between  $90^\circ$  and  $180^\circ$ , using the swiftest  $\alpha$  particles to test whether the ordinary law of force begins to break down even in the case of the heavy elements. This would give us valuable information as regards the dimensions of the nucleus and the nature of the forces in its neighbourhood. When we examine the results of a collision between an  $\alpha$  particle and a light nucleus like that of hydrogen, where the nuclei must approach very closely to each other, we obtain unequivocal evidence that the ordinary law of force no longer holds at the very small distances involved—about  $4 \times 10^{-13}$  cms. The experiments of the writer and of Chadwick and Bieler show that the number of hydrogen nuclei set in swift motion is much greater than is to be expected on the point-nucleus theory, while the change of number with velocity of the  $\alpha$  particle varies in the opposite way from that to be expected on simple theory. Such a wide departure between observation and theory is only explicable if we assume either that the nuclei have sensible dimensions or that the inverse square law of force entirely breaks down for such very close collisions. If we suppose the complexity in structure and in laws of force is to be ascribed to the  $\alpha$  particle rather than to the hydrogen nucleus, Chadwick and Bieler, as the result of a careful series of experiments, concluded that the  $\alpha$  particle behaved as if it were a perfectly elastic body, spheroidal in shape, with its minor axis  $4 \times 10^{-13}$  cms. in the direction of motion and major axis  $8 \times 10^{-13}$  cms. Outside this spheroidal region the forces fell off according to the ordinary inverse square law, but inside this region the forces increased so rapidly that a particle was reflected from it as from a perfectly elastic body. No doubt such a conception is somewhat artificial, but it does serve to bring out the essential points involved in the collision—viz. that when the nuclei approach within a certain critical distance from each other forces come into play which vary more rapidly than the inverse square. It is difficult to ascribe this breakdown of the law of force merely to the finite size of the nuclear structure, but it rather points to the presence of new and unexpected forces which come into play at such small distances. This view has been confirmed by some recent experiments of Bieler in the Cavendish Laboratory, in which he has made, by scattering methods, a detailed examination of the law of force in the neighbourhood of a light nucleus like that of aluminium. For this purpose he compared the relative number of  $\alpha$  particles scattered within the same angular limit from aluminium and from gold. For the range of angles employed, viz. up to  $100^\circ$ , it is assumed that the scattering of gold follows the inverse square law. He found that the ratio of the scattering in aluminium, compared with that in gold, depended on the velocity of the  $\alpha$  particle. For example, for an  $\alpha$  particle of 3.4 cms. range the

theoretical ratio obtained for angles of deflection below  $40^\circ$  was about 7 per cent. lower for an average angle of deflection of  $80^\circ$ . On the other hand, for swifter particles of range, 6.6 cms., a departure from the theoretical ratio was much more marked and amounted to 29 per cent. for an angle of  $80^\circ$ . In order to account for these results he supposed that close to the aluminium nucleus an attractive force is superimposed on the ordinary repulsive forces. The results agreed best with the assumption that the attractive force varied according to the inverse fourth power of the distance, and that the forces of attraction and repulsion balanced at about  $3.4 \times 10^{-13}$  cms. from the nuclear centre. Inside this distance the forces are entirely attractive, outside it they are repulsive.

While we need not lay too much stress on the accuracy of the actual value obtained or of the law of attractive force, we shall probably not be far in error in supposing the radius of the aluminium nucleus is not greater than  $4 \times 10^{-13}$  cms. It is of interest to note that the forces between an  $\alpha$  particle and a hydrogen nucleus were found to vary rapidly at about the same distance.

It thus seems clear that the dimensions of the nuclei of light atoms are small, and almost unexpectedly small in the case of aluminium, when we remember that 27 protons and 14 electrons are concentrated in such a minute region. The view that the forces between nuclei change from repulsive to attractive when they are very close together seems very probable, for otherwise it is exceedingly difficult to understand why a heavy nucleus with a large excess of positive charge can hold together in such a confined region. We shall see that the evidence from various other directions supports such a conception, but it is very unlikely that the attractive forces close to a complex nucleus can be expressed by any simple power law.

### RADIOACTIVE EVIDENCE.

A study of the long series of transformations which occur in uranium and thorium provides us with a wealth of information of the modes of disintegration of atoms, but unfortunately our theories of nuclear structure are not yet sufficiently advanced to interpret these data with any detail. The expulsion of high-speed  $\alpha$  and  $\beta$  particles from the radioactive nucleus gave us some idea of the powerful forces resident in the nucleus, for it can be estimated that the energy of emission of the  $\alpha$  particles is in some cases greater than the energy that would be acquired if the  $\alpha$  particle fell freely between two points differing in potential by about 4 million volts. The energies of the  $\beta$  and  $\gamma$  rays are on a similar scale of magnitude.

I have not time to discuss the details of these transformations, but will confine myself to the consideration of certain peculiarities of disintegration of the elements radium C, thorium C, and actinium C. Indubitable evidence has been obtained that these elements break up

in at least two distinct ways, giving rise to branch products. For example, thorium C emits two types of  $\alpha$  rays, 65 per cent. of range 8.6 cms. and 35 per cent. of range 4.8 cms., and in addition some  $\beta$  rays. In order to explain these results, it has been suggested that a fraction of the atoms of thorium C first break up with the emission of a  $\beta$  particle and the resultant product then emits  $\alpha$  rays. The other fraction breaks up in reverse order, first emitting an  $\alpha$  particle and the subsequent product a  $\beta$  particle. The dual changes in radium C and actinium C can be represented in a similar way, although the relative numbers of atoms in each branch vary widely for the different elements.

It has always been a matter of remark that, apart from uranium X, only the C bodies have been observed to give rise to branch products, and that their modes of disintegration should show so many points of similarity. Thus remarkable resemblance between radium C and thorium C, for example, has been still further emphasised by the discovery of Bates and Rogers of the existence of additional groups of  $\alpha$  particles. Radium C gives out groups of ranges in air, 7.0, 9.3, 11.2, and 13.3 cms., where thorium C gives out  $\alpha$  particles of ranges 4.8, 8.6, 11.5, 15.0, and 18.4 cms.

We can offer a possible explanation of this anomaly on the supposition that the  $\alpha$  and  $\beta$  particles which are liberated from these elements exist as satellites of a core or nucleus which is common to both elements. These satellites if in motion would be held in equilibrium outside the central core by the attractive forces arising from it, and these forces would be the same for both elements. On this view the manifestations of radioactivity are to be ascribed not to the main core, but to the satellite distribution, which will be somewhat different for the two elements.

Such a point of view provides a useful working hypothesis not only to account for the similarity in the modes of transformation of these two elements, but suggests a possible explanation of the liberation of a number of groups of  $\alpha$  particles having different energies. There are two ways of regarding this question. We may in the first place suppose that a certain amount of surplus energy has to be liberated in the disintegration, and that this energy may be given to any one of a number of satellites. There will be a certain probability that any particular particle will be given this energy, and on this will depend the relative number of particles in the different  $\alpha$  ray groups. The ultimate energy of ejection of an  $\alpha$  particle will depend on its position in the field of force surrounding the inner core at the moment of liberation. On the other hand, we may suppose that the same  $\alpha$  particle is always ejected, but that the particle may occupy in the atom one of a number of "stationary" positions analogous to the "stationary states" of the electron in Bohr's theory of the outer atom. This rests on the assumption that all the atoms will not be identical in satellite structure, but there will be a number of possible

"excited" states of the atom as a consequence of the previous disintegrations. This satellite theory is useful in another connection. Ellis has suggested that possibly the high-frequency  $\gamma$  rays from a radioactive atom may arise, not from the movement of the electrons as ordinarily supposed, but from the transfer of an  $\alpha$  particle from one level to another. In such a case the difference in energies between the various groups of  $\alpha$  particles from radium C and thorium C should be connected by the quantum relation with the frequencies of prominent  $\gamma$  rays. The evidence at present available is not definite enough to give a final decision on this problem, but points to the need of very accurate measurements of the energies of the various groups of  $\alpha$  particles. On account of the relatively small number of particles in some of the groups this is difficult of accomplishment.

In considering the satellite theory in connection with the radioactive bodies, it is at first sight natural to suppose, since the end-product of both the radium and thorium series is an isotope of lead, that one of the isotopes of lead forms the central core. It may, however, well be that the radioactive processes cease when there are still a number of satellites remaining. In such a case the core may be of smaller mass than the lead nucleus.

#### FREQUENCY OF VIBRATION OF THE NUCLEUS.

One of the most interesting and important methods of throwing light on nuclear structure is the study of the very penetrating  $\gamma$  rays expelled by some radioactive bodies. The  $\gamma$  rays are identical in nature with the X rays, but the most penetrating type of rays consists of waves of much higher frequency than can be produced in an ordinary X-ray tube. The work of the last few years has indicated very clearly that the major part of the  $\gamma$  radiation from bodies, like radium B and C, originates in the nucleus. A determination of the frequencies of the  $\gamma$  rays thus gives us direct information on the modes of vibration of parts of the nuclear structure. The frequency of some of the softer  $\gamma$  rays emitted by radium B and radium C were measured by the crystal method by Rutherford and Andrade, but it is difficult, if not impossible, by this method to determine the frequencies of the very penetrating rays. Fortunately, due largely to the work of Ellis and Fraulein Möstner, a new and powerful method has been devised for this purpose. It is well known that the  $\beta$  rays from radium B and radium C give a veritable spectrum in a magnetic field, showing the presence of a number of groups of  $\beta$  rays each expelled with a definite speed. It is clear that each group of  $\beta$  rays arises from conversion of the energy of a  $\gamma$  ray of definite frequency into a  $\beta$  ray in one or other of the electronic levels in the outer atom. The energy  $w$  required to move an electron from one of these levels to the outside of the atom is known from a study of X-ray absorption spectra. The frequency  $\nu$  of the  $\gamma$  ray is

thus given by the quantum relation  $h\nu = E + \omega$ , where  $E$  is the measured energy of the  $\beta$  particle.

Since each  $\gamma$  ray may be converted in any one of the known levels, electronic levels in the outer atom, a single  $\gamma$  ray is responsible for the appearance of a number of groups of  $\beta$  rays, corresponding to conversion in the K, L, M and N, etc., levels. In this way an analysis of the  $\beta$ -ray spectrum allows us to fix the frequency of the more intense  $\gamma$  rays which are emitted from the nucleus. The energy of the shortest wave measured in this way by Ellis corresponds to more than two million volts, while other evidence shows that probably still shorter waves are emitted in small quantity from radium C. Ellis and Skinner have shown that the energies of these rays show certain combination differences, such as are so characteristic of the energies of the X rays arising from the outer electrons. A series of energy levels may thus be postulated in the nucleus similar in character to the electrons levels of the outer atom, and the  $\gamma$  rays have their origin in the fall either of an electron or of an  $\alpha$  particle between these levels. This is a significant and important result, indicating that the quantum dynamics can be applied to the nucleus as well as to the outer electronic structure.

The probability of levels in the nuclear structure is most clearly seen on the satellite hypothesis, but in our ignorance of the laws of force near the core we are at the moment unable to apply the quantum dynamics directly to the problem. The outlook for further advances in this direction is hopeful, but is intimately connected with a further development of our knowledge of the laws of force that come into play close to the nucleus in the region occupied by the satellites.

#### ARTIFICIAL DISINTEGRATION OF ELEMENTS.

We have seen that it is believed that the nuclei of all atoms are composed of protons and electrons, and that the number of each of these units in any nucleus can be deduced from its mass and nuclear charge. It is, however, at first sight, rather surprising that no evidence of the individual existence of protons in a nucleus is obtained from a study of the transformations of the radioactive elements, where the processes occurring must be supposed to be of a very fundamental character. As far as our observations have gone, electrons and helium nuclei, but no protons, are ejected during the long series of transformations of uranium, thorium and actinium. One of the most obvious methods for determining the structure of a nucleus is to find a method of disintegrating it into its component parts. This is done spontaneously for us by nature to a limited extent in the case of the heavy radioactive elements, but evidence of this character is not available in the case of the ordinary elements. As the swift  $\alpha$  particle from the radioactive bodies is by far the most

energetic projectile known to us, it seemed from the first possible that occasionally the nucleus of a light atom might be disintegrated as the result of a close collision with an  $\alpha$  particle. On account of the minute size of the nucleus it is to be anticipated that the chance of a direct hit would be very small, and that consequently the disintegration effects, if any, would be observed only on a very minute scale. During the last few years Dr. Chadwick and I have obtained definite evidence that hydrogen nuclei or protons can be removed by bombardment of  $\alpha$  particles from the elements boron, nitrogen, fluorine, sodium, aluminium and phosphorus. In these experiments the presence of H nuclei is detected by the scintillation method, and their maximum velocity of ejection can be estimated from the thickness of matter which can be penetrated by these particles. The number of H nuclei ejected even in the most favourable case is relatively very small compared with the number of  $\alpha$  particles employed, viz. about one in a million.

In these experiments the material subject to bombardment was placed immediately in front of the source of  $\alpha$  particles, and observations on the ejected particles were made on a zinc-sulphide screen placed in a direct line a few centimetres away. Using radium C as a source of  $\alpha$  rays, the ranges of penetration, expressed in terms of centimetres of air, were in all these cases greater than the range of free nuclei (30 cms. in air) set in motion in hydrogen by the  $\alpha$  particles. By inserting absorbing screens of 30 cms. air equivalent in front of the zinc-sulphide screen, the results were quite independent of the presence of either free or combined hydrogen as an impurity in the bombarded materials. Some of the lighter elements were examined for absorptions less than this, but in general the number of  $\alpha$  particles due to hydrogen contamination of the source and the materials was so large that no confidence could be placed in the results:

In such experiments many scintillations can be observed, but it is very difficult to decide whether these can be ascribed in part to an actual disintegration of the material under examination. The presence of long-range particles of the  $\alpha$ -ray type from the source of radium C still further complicates the question, since in general the number of such particles is large compared with the disintegration effect we usually observe.

To overcome these difficulties, inherent in the direct method of observation, Dr. Chadwick and I have devised a simple method by which we can observe with certainty the disintegration of an element when the ejected particles have a range of only 7 cms. in air. This method is based on the assumption, verified in our previous experiments, that the disintegration particles are emitted in all directions relative to the incident rays.

A powerful beam of  $\alpha$  rays falls on the material to be examined and the liberated particles are observed at an average angle of  $90^\circ$  to

the direction of the incident  $\alpha$  particles. By means of screens it is arranged that no  $\alpha$  particles can fall directly on the zinc sulphide screen.

This method has many advantages. We can now detect particles of range more than 7 cms with the same certainty as particles of range above 30 cms. in our previous experiments, for the presence of hydrogen in the bombarded material has no effect. This can be shown at once by bombarding a screen of paraffin wax, when no particles are observed on the zinc sulphide screen. On account of the very great reduction in number of H nuclei or  $\alpha$  particles by scattering through  $90^\circ$ , the results are quite independent of H nuclei from the source or of the long-range particles found by Bates and Rogers. The latter are just detectable under our experimental conditions when a heavy element like gold is used as scattering material, but are inappreciable for the lighter elements.

A slight modification of the arrangement enables us to examine gases as well as solids.

Working in this way we have found that in addition to the elements boron, nitrogen, fluorine, sodium, aluminium, and phosphorus, which give H particles of maximum range in the forward direction between 40 and 90 cms., the following give particles of range above 7 cms.: neon, magnesium, silicon, sulphur, chlorine, argon, and potassium. The numbers of the particles emitted from these elements are small compared with the number from aluminium under the same conditions, varying between  $1/3$  and  $1/20$ . The ranges of the particles have not been determined with accuracy. Neon appears to give the shortest range, about 16 cms. under our conditions, the ranges of the others lying between 18 cms. and 30 cms. By the kindness of Dr. Rosenhain we were able to make experiments with a sheet of metallic beryllium. This gave a small effect, about  $1/30$  of that of aluminium, but we are not yet certain that it may not be due to the presence of a small quantity of fluorine as impurity. The other light elements, hydrogen, helium, lithium, carbon, and oxygen, give no detectable effect beyond 7 cms. It is of interest to note that while carbon and oxygen give no effect, sulphur, also probably a "pure" element of mass 32, gives an effect of nearly  $1/3$  that of aluminium. This shows clearly that the sulphur nucleus is not built up solely of helium nuclei, a conclusion also suggested by its atomic weight of 32.07.

We have made a preliminary examination of the elements from calcium to iron, but with no definite results, owing to the difficulty of obtaining these elements free from any of the "active" elements, in particular nitrogen. For example, while a piece of electrolytic iron gave no particles beyond 7 cms., a piece of Swedish iron gave a distinct effect which was undoubtedly due to the presence of nitrogen, for after prolonged heating *in vacuo* the greater part disappeared. Similar results were experienced with the other elements in this

region. A number of elements of higher atomic weight have been examined in a preliminary way, but in no case have we observed any very definite evidence of disintegration under our experimental conditions.

Recently Kirsch and Petterson, working in the Radium Institute, Vienna, have examined the number of the lighter elements for evidence of disintegration, using the direct method referred to (see *Nature*, Sept. 15, Nov. 10, 1923; *Phil. Mag.*, March 1924). Special types of source were employed, and special care taken to purify the bombarded materials from hydrogen. They concluded that they had obtained evidence of the disintegration of magnesium, silicon and beryllium. The ranges of the particles from magnesium and silicon were, however, much shorter (13 cms. and 12 cms. respectively) than we have observed in our experiments, while the numbers of particles observed were much greater. The effect obtained from beryllium, using the oxide as a source, was apparently much larger than the very small effect we found in beryllium metal by our method of observation. We must await the results of further experiments to see whether these conflicting results can be reconciled.

In considering the results of our new and old observations some points of striking interest emerge. In the first place, all the elements from fluorine to potassium inclusive suffer disintegration under  $\alpha$ -ray bombardment. As far as our observations have gone, there seems little doubt that the particles ejected from all these elements are H nuclei. The odd elements B, N, F, Na, Al, P, all give long-range particles varying from 40 cms. to 90 cms. in the forward direction; the even elements C, O, Mg, Si, S either give no particles at all, as in the case of C and O, or give particles of much less range than the adjacent odd-numbered elements. The difference between the ranges of even and odd elements becomes much less marked for elements heavier than phosphorus.

This obvious difference in velocity of expulsion of the H nuclei from even and odd elements is a matter of great interest. Such a distinction can be paralleled by other observations of an entirely different character. Harkins has shown that elements of even atomic number are much more abundant in the earth's crust than elements of odd number. In his study of isotopes Aston has shown that in general odd-numbered elements have only two isotopes differing in mass by two units, while even-numbered elements in some cases contain a large number of isotopes. This remarkable distinction between even and odd elements cannot but excite a lively curiosity, but we can at present only speculate on its underlying cause.

[E. R.]



Friday, April 11, 1924.

J. MITCHELL BRUCE, Esq., C.V.O. M.D. LL.D.,  
Manager and Vice-President. in the Chair.

JOCELYN FIELD THORPE, C.B.E. D.Sc. F.R.S.,  
Professor of Organic Chemistry, Imperial College of Science  
and Technology.

### Colours, Stains, and Dyes.

THE great majority of chemical substances occurring either as natural products or as the outcome of synthetic preparations in the laboratory are colourless. In other words, white light reflected from their surfaces or transmitted through these solutions is unaffected so far as its balanced colours are concerned, and emerges unaltered. The absorption of light in these cases is general; that is, it takes place equally throughout the visible range of the spectrum and the object, therefore appears colourless.

On the other hand, there are a number of substances which possess the property of absorbing certain portions of the visible spectrum while reflecting or transmitting the remainder. These substances, therefore, appear to the eye to be coloured in accordance with the portion of the spectrum transmitted or reflected. A red substance is one which absorbs the blue region of the spectrum; a blue substance one which absorbs the red region, and so forth. This is known as selective absorption. Again, there are a number of substances, chiefly members of the carbon family, which have the power of absorbing rays outside the visible region of the spectrum—for example, in the infra-red or the ultra-violet—and these substances, since they possess selective absorption, must be regarded as coloured in a chemical sense, although the “colour” they transmit or absorb is not visible to the eye.

The hydrocarbon benzene is an example of the type of chemically coloured substance, and, as we shall find later, this property possessed by benzene causes it to be the parent substance of those very numerous and industrially important materials—the coal-tar dyes.

It is not in its lack of power to detect the ultra-violet range alone that the eye fails as an organ of vision, because even in the visible

region its power to detect the end colours is seriously restricted. It is most sensitive towards green and red.

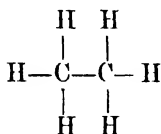
The power of a chemical substance to produce selective absorption is without doubt due to its chemical structure—that is to say, white light is “filtered” through the molecular structure of the substance, leaving a “portion” behind in its passage. The colour is therefore dependent on the chemical composition of the particular compound. On the other hand, it is possible to produce visible colour by entirely physical or mechanical means, as, for example, by ruling a number of fine lines on glass, and in these cases colour is independent of chemical structure, being entirely physical in character.

Nature, in producing the variety of coloured substances around us, has adopted both the physical and chemical methods to achieve her ends. The colour of flowers and leaves has been brought about by the use of coloured chemical substances, and these I shall deal with later. But many of the colour effects produced in the wings and feathers of birds and in butterflies are not due to the presence of any coloured substance in them, but to the arrangement of fine filaments or hairs, which serve the purpose of disintegrating white light and reflecting the desired shade of colour. The best test for this kind of colour effect is to examine the coloured object by transmitted light. If no colour is transmitted the reflected colour is probably due to physical causes.

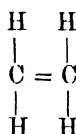
A considerable number of the chemical substances which owe their colour to structure are inorganic in origin, and the colours depend mainly on the presence of some colour-producing metal; for example, chromium, cobalt, copper, and so forth. They are mostly used as pigments for the production of coloured surfaces by painting, or for the production of coloured decorations on china. Of these I do not propose to make any mention, not because they are unimportant as coloured substances, but because they do not trace any relationship to the stains and dyes which belong to organic chemistry, and are bound up with the recurrence of one particular element, namely, carbon.

There are some 300,000 definite compounds of carbon known, and the activities of research chemists add, perhaps, 4000 to these yearly. The majority of these compounds are colourless in the sense that they give only general absorption throughout the visible region of the spectrum. Some are, however, coloured—that is, they give selective absorption within the visible region—and it is evident that in these cases the colour cannot be ascribed to the presence of some particular metal, as with the metallic pigments, but must be due to some special condition of the element carbon. As a matter of fact, it is due to what is known as the “unsaturated state.” The greater number of known compounds of carbon are “saturated” in the sense that all affinity which the carbon atom possesses for the atoms

of other elements is fully satisfied. This is the case when carbon combines with hydrogen to form methane  $\text{CH}_4$ , or when it combines with oxygen to form carbon dioxide ( $\text{CO}_2$ ). No carbon compound of this type possesses colour, and every "saturated" compound shows general absorption of light. It is possible, however, to cause carbon to combine with carbon by more than one valency, and in such a case a condition of "unsaturation" arises :



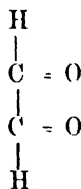
Ethane (saturated).



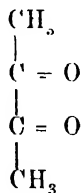
Ethylene (unsaturated).

The affinity of each carbon atom is no longer satisfied by its proper quantity of hydrogen (or oxygen), and since there is naturally always a tendency for the substance to acquire the hydrogen atoms necessary for saturation, the "unsaturated" condition is definitely less stable than the saturated state.

The presence of one unsaturated linkage does not, however, confer colour on an organic compound – at least two being necessary for the purpose. It is also necessary that the two double linkages should be separated by one single linkage. This is known as the conjugated system of double linkages, and its presence in an organic compound apparently confers on it the property of producing selected absorption in the visible region of the spectrum. The simplest possible coloured organic substances are therefore glyoxal and diacetyl :



Glyoxal.



Diacetyl.

These substances, however, although they are of great interest as showing the origin of colour in organic substances, are relatively unimportant owing to their slight colour and their rarity. It is to the derivatives of the hydrocarbon benzene, upon which is based the chemistry of the coal-tar colour, that special interest attaches.

As already mentioned, benzene shows selective absorption in the ultra-violet region of the spectrum, and is therefore visibly colourless, although, chemically speaking, it possesses marked colour. The

great number of the derivatives of benzene are, therefore, visibly colourless, but the chief point which has to be remembered is that, although visibly without colour, these derivatives possess potentially visible colour, and it is always possible to produce visibly coloured substances from them by modifying the molecular conditions which lead to the selective absorption causing visible colour.

The organic chemist's conception of the structure of benzene is still that which was propounded by Kekulé some seventy years ago, and it is fair to say that no theory, either physical or chemical, has been brought forward since then which can be regarded as quite adequate. Kekulé regarded benzene as a substance containing a conjugated system of double linkages, upon which the colour of organic substances depends; but in order to account for the peculiar properties of benzene, its remarkable stability, and the formation of its derivatives, it is necessary to postulate a symmetrical formula which is expressed either by the Armstrong formula or by the simple hexagon—a necessity, which was met by Kekulé by the supposition that there was rapid dynamic interchange between the two unsaturated individuals of his formula. Below are given the forms of linkages which have been given to the benzene molecule, the carbon atoms, assumed to occur at the points of the hexagon, being omitted:



Kekulé (I).



Kekulé (II).



Armstrong.



Conventional form.

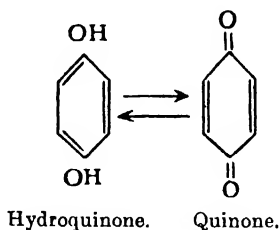
This dynamic interchange, leading to symmetry, is expressed both by the Armstrong formula and by the conventional formula, but it is evident that each of them is merely a compromise, and represents an intermediate condition between two rapidly interchanging forms. They do not mean more than this, because any condition which postulates the existence of trivalent carbon has to contend with a number of cases in which the occurrence of this condition leads to instability quite out of keeping with the remarkable stability of benzene and its analogues and derivatives. This is the case with triphenylmethyl and similar compounds.

The dynamic conception of the structure of benzene supplies a reason for the recurrence of the strong ultra-violet absorption which is characteristic of this substance. Moreover, it suggests that if it were possible to modify the conditions leading to this absorption, it might be possible to throw the absorption within the visible range of the spectrum, and thus produce visible colour.

The simplest visibly-coloured member of the series is quinone,



which is produced easily from hydroquinone by oxidation and is reconverted into hydroquinone on reduction :



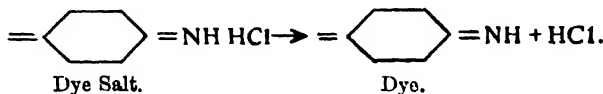
Here, then, at any rate, we have one means by which we can produce visible colour from a benzene derivative. There are certainly other means, but these are not as yet so clearly defined, and there is no question that when H. E. Armstrong propounded his quinone theory of colour he enunciated the fundamental principle on which the chemistry of the coal-tar colours is based. For there can be no doubt that the colours of these compounds are due to the presence in them of a quinone residue, which, acting like the simplest quinone ring shown above, throws the ultra-violet absorption of the visibly colourless benzene derivative into the visible region of the spectrum.

This is easily shown by the conversion of the visibly colourless phenolphthalein into its coloured alkali salt. However, it is a simple matter by altering the groups present to throw the absorption into any portion of the visible spectrum required, and thus to obtain any desired colour. The chemist is able, therefore, while retaining the same skeleton, to produce any colour at will by merely altering the nature of attached groups.

The name coal-tar colour is derived, of course, from the fact that the parent hydrocarbons from which the colours are derived—the benzene hydrocarbons and their analogues—are obtained by the distillation of coal-tar. The first of the series, mauveine, was discovered by the late Sir William Perkin in 1856, in an attempt to prepare the alkaloid quinine synthetically. But Perkin did more than discover a new series of colouring matters. He also introduced a new method of dyeing. Up to that time dyeing had been a composite process involving the actual formation of the coloured substance on the fibre itself. The two chief processes in use were (*a*) that of vat-dyeing, and (*b*) that of mordant dyeing. The first, represented by indigo dyeing, involved the reduction of the coloured substance (indigo) to indigo-white, a material soluble in alkali; the steeping of the fibre in the solution; and the reproduction of the insoluble dye by means of the oxygen of the air. The second required the previous impregnation of the fibre with a metallic hydroxide and the subsequent formation of a coloured lake on the

fibre by steeping the prepared material in a dyestuff (alizarine) capable of yielding such a lake

In each case, therefore, two distinct processes were involved. In the process introduced by Perkin only one operation was necessary. The dye contains, as already mentioned, a quinone or quinonimine residue, which causes the dyestuff in the form of its salt to be soluble in water :



It happens that the coloured base is soluble in the wool fibre, and when the fibre is added to the dye-bath the coloured base is extracted, leaving the mineral acid free in solution. The operation is of the same order as that which determines the extraction by, say, ether of an organic substance soluble in water. The coloured base is not, however, soluble in cotton, and hence this material is not coloured in the dye-bath.

These are known as the basic dyes; and a similar effect is produced by the acid dyes, although, since these are the sodium salts of sulphonic acids, the dye-bath has to be rendered acid previously in order to liberate the free sulphonic acids, which then dissolve in the substance of the wool. Cotton would not, of course, be coloured by this process, although, as it was found that the new basic colours possessed the power of giving an insoluble coloured compound with tannic acid and an antimony salt, it was possible to affix them to the cotton fibre by a two-process method, involving the previous treatment of the material with tannic acid and tartar emetic.

It was not until twenty years later that it was found (Böttger, 1886) that a certain type of azo-dye derived from benzene possessed the property of being soluble in the cotton fibre, a discovery which led to the preparation of the large number of substantive cotton dyes known at the present day. In this case it is the sodium salt of the sulphonic acid which is extracted. This discovery was entirely accidental, but, as so often happens in organic chemistry, it was found that the property was possessed by a large number of substances of the same type, or having the same skeleton formation, and since it is possible readily to alter the shade by varying the nature of attached groups, the series contains representatives of all shades of colour.

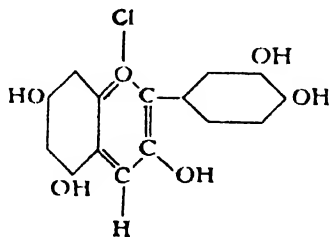
It must be remembered, however, that there is a marked difference between the two methods of dyeing—one, the older method, in which the dye is formed in the fibre, and the other, the newer method, in which the fibre acts merely as an extractor for the coloured base, acid, or salt. It is evident that, other things being equal, the older processes should give the faster dyeings—that is, the colour would

be more firmly fixed in the fibre and less likely to be affected by the various conditions, such as exposure to light, washing, etc., to which a dyed fabric has usually to be subjected. This is, as a matter of fact the case, and numerous processes have been devised by which the stained fabric (as I prefer to call it) can be rendered more fast by after-treatment—that is to say, by causing another colour to be produced in the fibre from the colouring matter already there. One of the best illustrations of this is the method by which an azo-dye can be produced on the fibre from a stained fabric which has been stained by a substance having an  $\text{NH}_2$  group :



There are many other methods, such as after-treatment with metallic salts, or with formaldehyde, which can be employed. Indeed, such processes would be still more necessary were it not for the remarkable tenacity with which the stained fabric, in many cases, retains its stain. The affinity varies in different cases, both as regards the power and speed of absorption, and is probably connected with the size of the molecular (colloidal) aggregates which are present in the dye-solutions. It is not connected with the actual molecular weights.

Nevertheless, although there are some stains which possess so marked an affinity for the fibre as to render them comparable with true dyestuffs (those produced on the fibre) in fastness, and some which lend themselves to after-treatment, and fall therefore within the category of true dyestuffs, there are a large number which possess all the inherent disabilities of the class—that is, they are unsaturated organic compounds tending to pass into the saturated (colourless) state under favourable conditions. Such conditions are always present in the oxygen of the air, which in the presence of light constitutes a formidable opponent to all coloured organic compounds. As already mentioned, Nature got over this difficulty in the case of bird's feathers and butterfly's wings, and also in the wing cases of coloured beetles, by ignoring the organic colour altogether. She utilised them, however, in the case of the flowers, but chose substances highly oxygenated in structure, which would be least likely to be affected by air and light. For example, the colour of the red rose is delphinidine



and this is also the basis of the colour of the blue cornflower, the only difference being in the character of the group attached to the oxonium oxygen.

However, as the science of organic chemistry advanced, it became possible to contemplate the synthetic preparation of some of the natural colouring matters, of which indigo, alizarine, and logwood were types. These are not natural colouring matters in the sense that they are used by Nature as such, but have been evolved by man for his own purpose by a process of trial and error. They represent the survivors of a vast number of natural substances with which man must have experimented throughout the ages in order to produce colour for his own purposes. Together with certain mordant colours derived from lichens, which are still used for dyeing in certain parts of the country, they constituted the sole means of producing dyed fabrics at the time when the coal-tar colours were discovered. Their value as dyestuffs was without question, the world's yearly consumption of indigo alone, at that time, representing some 4,000,000/.

It must also be remembered that it was not the question alone of the commercial production of the dye in competition with the natural product which was sought, because this must have appeared a totally impracticable problem in those early days. It was rather the search for the reason why alizarine was a mordant dye and why indigo was a vat-dye which was the incentive to research, because when these facts were discovered other substances having similar properties could be prepared. The attack in every case followed the usual lines. In the first instance, the structure of alizarine (the mordant dyestuff of the madder root) was revealed by analysis, when Baeyer found that it gave anthracene on distillation with zinc. Its synthesis from the anthracene of coal-tar followed in the next year, being effected almost simultaneously by Graebe and Liebermann in Germany, and by Perkin in England. In this case the preparation was so simple and the raw material so easily obtained that the natural madder industry was rapidly killed. The determination of the formula and synthesis of

alizarine showed the particular grouping, namely,  $\begin{array}{c} \text{CO} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{OH} \end{array}$ , on which mordant dyeing depended. Hence the preparation of a large number of analogues of varying shades of colour followed.

The determination of the structure of indigo took longer, and occupied Baeyer at Munich some eighteen years. In this case the colour was synthesised and manufactured on a commercial scale three years before its structure was determined, because, as sometimes happens, a reaction, the course of which was then unknown, led to the formation of the dye. Here, again, the determination of structure showed that the property of vat-dyeing depended on the presence

of the grouping  $\begin{array}{c} \text{CO} \\ | \\ -\text{C}=\text{C}- \end{array}$ , and in consequence, whereas blue



indigo was the only known member of its class in 1890, at the present day every shade of colour is represented in this particularly fast series.

Finally, at the beginning of the present century, the accidental discovery of Indanthrene by Bohr placed on the market the first member of a series of vat-dyes which constitutes without question the fastest series of colouring matters hitherto prepared. Practically all shades of colours are represented, the principle of dyeing being essentially the same as that of indigo.

Before the War we relied mainly on Germany for the production of our dyestuffs, and, what was still more serious, we left to them the research work on which the production of new dyestuffs depended. Dyestuff chemistry is merely a branch of organic chemistry, which includes also the preparation of organic chemical substances used in a variety of industries essential in peace and war. The possession of a dyestuff industry implies, therefore, the possession of a band of trained organic chemists, and, what is more important, the possession of University and University College Laboratories, where organic chemists can be adequately trained in methods of research. As a member of the Dyestuffs Development Committee it has been my good fortune within the past six months to visit all the dye producing factories operating in Great Britain, and I have been struck with the very real success which has attended the efforts of the past five years to establish the industry. If we had merely reached the level of excellence attained in Germany before the War, the fact would have been very creditable, but we have done more than this, and in several cases, notably in the production of a new indanthrene green, we have already drawn ahead ; a position, it is to be hoped, we shall not again lose.

[J. F. T.]

Friday, June 6, 1924.

SIR ARTHUR KEITH, M.D. LL.D. F.R.S., Secretary and  
Vice-President, in the Chair.

LORD RAYLEIGH, Sc.D. F.R.S. M.R.I.

### The Glow of Phosphorus.

THE discovery of phosphorus was one of those which is associated with the transitional period when magic and science flourished to some extent side by side, and when the borderline between them was not very well defined. It seems to have been discovered by the alchemist Brand, of Hamburg. But in those days scientific discoveries were often cherished as valuable secrets, not so much for their commercial value as for the sense of superior knowledge and power which their exclusive possession was supposed to give. Scientific secrets are sometimes jealously guarded now, but not for this reason. When reticence is observed it is for the less romantic motive of commercial advantage. In the absence of this motive, the scientific men of to-day tell all they know, and tell it without delay.

The subject of phosphorus emerged into daylight in 1678, when Kunkel, who had learnt the secret by word of mouth, made it public. In 1780 the Hon. Robert Boyle deposited a paper on the same subject with the Royal Society. He had worked it out anew, without more than the hint that phosphorus came from an animal source.

It was a long time before the nature of the luminosity of phosphorus was finally settled. The early investigators not unnaturally classed it with the substances which become luminous by exposure to light, such as impure calcium sulphide. This notion survives in the word "phosphorescence," which is after all purely descriptive of the property of giving light. Now, however, the word is usually reserved for the cases like calcium sulphide. Phosphorus is not commonly spoken of as phosphorescent; its luminosity, as everyone now knows, is due to slow combustion in the oxygen of the air. It took a long time to prove this, and the question was still in a measure open down to the year 1874. The doubt arose partly from the extremely small quantity of oxygen necessary to make the phosphorus visibly luminous. Accidental leakages may thus confuse the question. Another puzzling circumstance was that when oxygen was substituted for air the glow was extinguished. This made it

difficult at first sight to defend the position that oxygen was what was wanted to make the phosphorus glow. I have sometimes thought that it might make a plausible argument for the homeopathist. The less oxygen you put in the more effect it seems to have. I will show you this. We have here a large flask of 4-litre capacity. There is phosphorus on the bottom, and in order to dissolve some of the phosphorus, and distribute it over a large area, some olive oil has been placed on it. I can swill this oil over the surface, so that it covers a large area. At present the flask is full of oxygen, and when the lights are extinguished you can see that the phosphorus is quite dark. We will now remove some of the oxygen by means of an air-pump, and you can see that the phosphorus suddenly blazes out at a lowered oxygen pressure. The same result may be shown by substituting air for oxygen.

This is not the only peculiar thing about the behaviour of glowing phosphorus. I will show you another. I have here a glass dish, with the oily solution of phosphorus which was used before covering the bottom. I remove the cover, and agitate it well, so as to bring the phosphorus in contact with air, and get vigorous oxidation and a good glow. I now hold above it a piece of cotton wool moistened with bisulphide of carbon. I do not squeeze the cotton wool so as to allow liquid drops to fall from it. I merely hold it loosely, so that the vapour can stream down from it on to the glowing surface. You can see that this vapour has an almost magical effect. It stops the phosphorus glowing altogether. If we allow a little time, the small quantity of vapour gets dissipated, and the phosphorus glows again.

Bisulphide of carbon is only one example of many vapours which will behave in this way. Ammonia, camphor, ethylene, turpentine, and essential oils generally, will do the same thing, though they vary widely as to their effectiveness. The majority of permanent gases have little effect in this way though I am not prepared to say what they might do at high pressures.

It will probably be admitted on consideration that the action of oxygen, which I showed you at first, is not essentially different from that of the other inhibiting substances. As will be explained shortly, the action occurs between oxygen and phosphorus vapour. A little oxygen is necessary to unite with the vapour as it comes away from the phosphorus surface, but the density that is of any use in this way is very small. If, for instance, we have a millimetre of oxygen pressure there will be in the gas space many oxygen molecules for one phosphorus molecule, and a further increase can hardly promote the combustion. The action of a great excess of oxygen, as when we admit it up to atmospheric pressure, must be something quite different. There is therefore no real paradox in the quenching by an excess of oxygen. Perhaps this analog. may help to explain what I mean : A man cannot live without water ; if he does not get

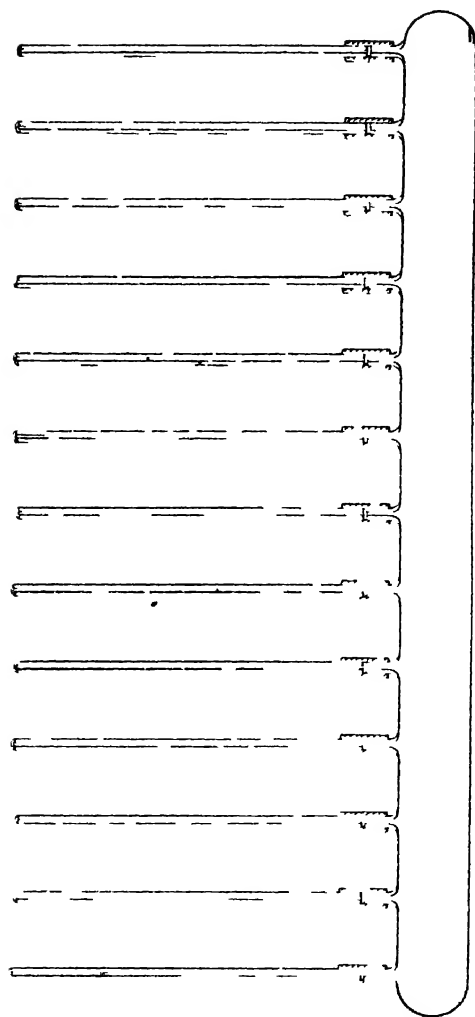


FIG. 1

it he will die of thirst; yet if he swallows too much he may be drowned. The water acts in quite different ways in the two cases, and so does oxygen in contact with phosphorus.

Another very strange thing happens when phosphorus is used to get rid of the last traces of oxygen in gas analysis. Suppose that we start with air in a confined space, and put a piece of phosphorus into it. At first the light is confined to the surface, but as the oxygen approaches exhaustion, the light is seen to become diffused throughout the volume of the vessel. It is easy to understand why this happens. Phosphorus is appreciably volatile at the ordinary temperature. When the surrounding oxygen is abundant it snaps up the phosphorus vapour at once, before it can diffuse away from the surface. But when oxygen becomes scarce the phosphorus has the chance to get some distance before this happens. This much is easy to understand. But if we look closely we see that the glow is not steady, but shows moving clouds of luminosity, most curious to watch.

Unfortunately, this experiment is too faint for an audience. But anyone can readily try it for himself. Nothing more is required than a piece of phosphorus stuck on a wire and introduced into a bottle - say, an ordinary bedroom decanter which stands inverted with its neck under water.

My own work on the subject started from this experiment, which I tried to develop into something more definite than clouds of vague outline moving in an ill-defined path. The slide (Fig. 1) shows an attempt in this direction which had some success.

The idea was to constrain the luminosity to move in one direction only. The horizontal tube has a layer of phosphorus lying along the bottom. The long narrow vertical tubes allow air to slowly leak in. When the oxygen originally in the tube is nearly exhausted, luminous pulses are seen to spring into existence at the side openings, to divide, and to travel along the tube. Usually this happens predominantly at one or two particular places. Pulses travelling along the tube in opposite directions kill one another when they meet.

I set up this arrangement in a dark room, and watched it from time to time. The experiment is so fascinating that one is tempted to waste a good deal of time in doing this. But after the lapse of a week or more a change was noticed. Although nothing had been touched, the movements were less lively, and the light had become stationary in places. Finally, all movement ceased.

What could be the explanation of this? The phosphorus had originally been melted into the tube under water, for safety, and the water was as far as possible poured off. But of course, it could not be got rid of completely in that way. The oxides of phosphorus produced by the combustion are greedy of water, and thus had gradually dried the tube. On adding water the movements began again.

The next slide (Fig. 2) shows a similar tube, with only one capillary entrance at the middle. It was dried out on the mercury pump in the first instance, and filled with nitrogen. A perfectly steady cloud of luminosity is seen when atmospheric oxygen begins to mingle with phosphorus vapour. *a*, *b* and *c* show successive stages as the oxygen influx is increased. If a drop or two of water is added we get a succession of luminous pulses starting up at the side entrance, dividing, and travelling in opposite directions along the tube (Fig. 2, *d*).

Now, what are we to think of these travelling pulses? Why does the luminosity move when there is water, and remain steady when there is none?

It is evident that the travelling pulses represent the propagation of a wave of chemical action along the tube. There is a mixture of oxygen and phosphorus-vapour ready to unite. It does not at once do so, but chemical union is determined by the passage of the wave, just as in the firing of a train of gunpowder.

Nothing of this kind seems, however, to happen in the absence of water. Union occurs at once in that case, the phosphorus being consumed as soon as oxygen comes near it. The water holds up the combustion.

Now that matters have been brought to this point, you will not fail to be reminded of the experiment which I showed you before, when phosphorus was prevented from glowing by the presence of bisulphide of carbon vapour. Water, it is evident, acts like the other inhibiting substances, but less powerfully. This naturally suggests that we might get the travelling pulses on a more impressive scale by using a more powerful inhibitor than water. It is not desirable to have too powerful an inhibition, however, and I have found that camphor succeeds as well as anything. We have here a long horizontal glass tube with a mixture of camphor and phosphorus lying on the bottom. The tube is exhausted with an air pump, and air is allowed slowly to leak into it through a fine adjustment valve at one end. You will see bright luminous flashes pass down the tube at short intervals. The camphor vapour holds up the combustion until enough air has leaked in to make a mixture of favourable composition, the combustion starts, and the wave is propagated.

The period will evidently depend on how strong is the inhibiting action. I have used ammonia as a convenient inhibitor for illustrating this, for we may make its action as powerful as we please by using a more concentrated solution. The period of the flashes is increased accordingly.

If you have followed me so far, you will I hope have been convinced that the moving clouds of luminosity observed when the absorption of oxygen by phosphorus is nearly complete, are linked up quite naturally with the existence of inhibiting substances.

I shall now direct your attention to another series of experiments

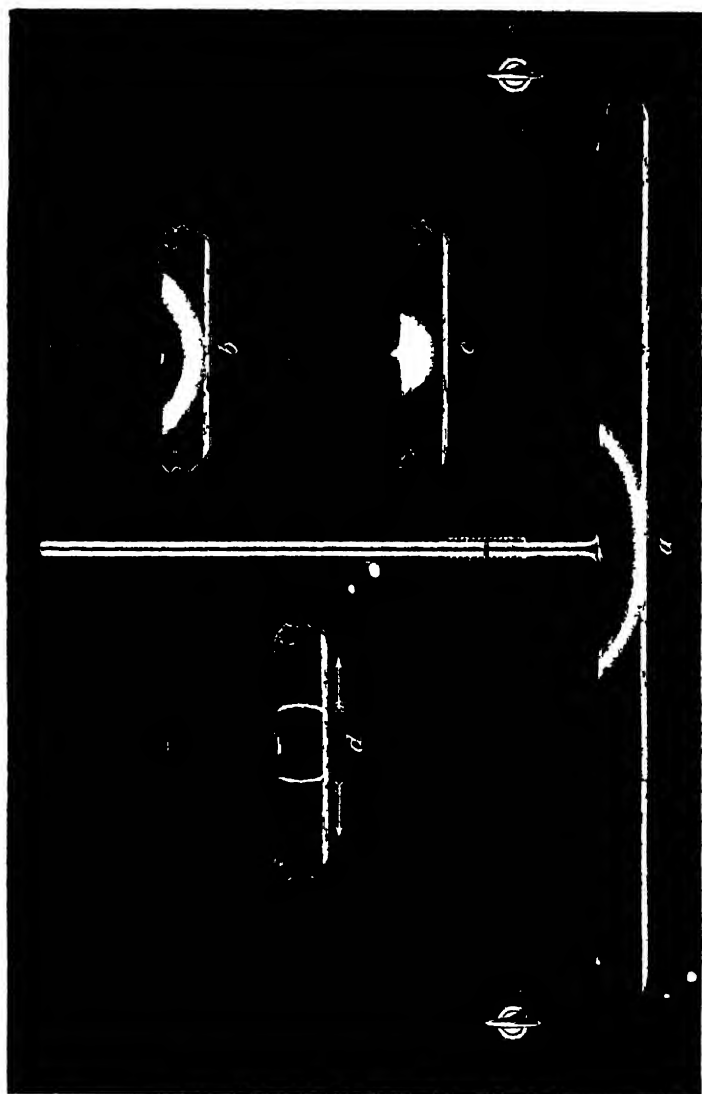
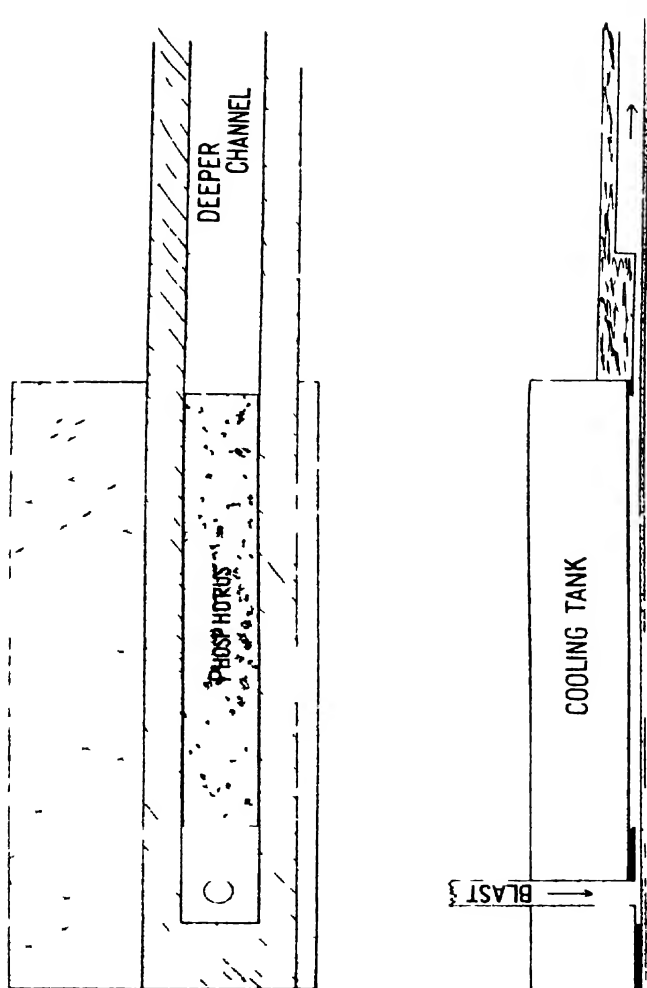


FIG. 2.





which allow a further unification of the same kind. They began with the repetition of an interesting observation by L. and E. Bloch, which showed that if some phosphorus was placed in a glass tube it was possible to blow the glow away from it by a blast of air, and maintain it at a distance downstream. In this form I found the experiment rather difficult of control, sometimes succeeding and sometimes failing, for no very apparent reason. It all turned out ultimately to be a matter of temperature, a few degrees making the whole difference. The next slide (Fig. 3) shows the arrangements which were made to bring this under satisfactory control. The phosphorus is a thin flat strip, cast into a suitable recess in the side of a water tank; thus its temperature cannot differ much from that of the water. The latter can be varied at pleasure by the use of ice or warm water. A flat sheet of glass is held at a distance of a millimetre or two parallel to the phosphorus slab, and the air flows between the two, being confined by suitable backing strips at the sides. The channel is prolonged downstream of the phosphorus, and is much suddenly deeper about two inches down. I should have liked to show you these experiments, but unfortunately they are not bright enough for an audience of more than five or six people, who can get quite close.

We must therefore be content with the photographs (Fig. 4, A and B). No. 1 shows how the phosphorus surface looks without any blast. V shows the glow blown right off, and maintaining itself downstream, where the channel is deepened. The dotted line (inked in on the photograph) shows the position of the phosphorus slab, which is quite dark. This is essentially the Blochs' original experiment. Interesting as it is, however, it by no means exhausts what we can learn with the arrangement described.

I examined the effect of changes of temperature, adjusting the blast in each case so that the glow was blown half-way down the phosphorus strip. The velocity of blast necessary to do this was found to diminish enormously as the temperature was reduced. Thus in cooling from room temperature to near the freezing-point, the velocity diminished a thousand times. I next tried altering the oxygen content, and found to my astonishment that enriching the air with oxygen had the same effect as cooling, and diminished the necessary velocity of blast in an equally striking degree. In both these cases the ultimate result, when the velocity had been reduced to something of the order of 1 cm. per second, was to make the glow flickering and uncertain of maintenance. On cooling a little more, or adding a little more oxygen, it went out altogether.

Now we must remember a fact, often enough insisted upon nowadays, that motion is relative. We have thought so far of the blast acting on the stationary cloud of luminosity, but we might equally regard the cloud of luminosity as propagating itself in the reversed direction through still air. When the air is much enriched

with oxygen the necessary blast is gentle—in other words, the propagation is slow. It appears then that *extinction is the limiting case of slow propagation*. If we can trace the cause of slow propagation the cause of extinction will not be far to seek.

Before passing to this, however, I wish to draw attention to some curious effects met with in the course of these experiments on the blast. The same sequence of changes occurs whether we reduce the temperature or increase the oxygen content. I shall suppose, for definiteness, that the latter course is followed. When the oxygen is very little the glow tends to cling to particular spots, from which it cannot readily be detached. II shows this to some extent, though other experiments were made in which it was much more striking. On close examination it appeared that these special spots were depressions in the phosphorus surface, when there was partial shelter from the blast. At these places the glow started, and when once started, it infected the gas down-stream of it, and made the blowing away impossible. VI shows this very clearly. In this case a hole was made intentionally.

As we increase the oxygen content a bright luminous head develops, followed by a darker space, and then uniform luminosity. This bright head no doubt represents the combustion of the stock of phosphorus vapour accumulated as the blast passes over the dark surface.

The next stage, IV, is observed when the blast is so rich in oxygen that extinction is near. You see that a succession of bright heads has now developed. They are separated by dark spaces. This photograph was given four hours' exposure, and was not easily obtained: for some movement of the luminous heads is difficult to avoid during so long a time by eye observation. The heads were seen quite regularly distributed along the column. The confusion on the right-hand side is due to unavoidable shifts

I could only attempt an imperfect explanation of these complex effects, shown in IV, and I will not trouble you with it on this occasion. Let us limit ourselves to the question of why propagation should occur at all, and why it should be slower when excess of oxygen is present.

In the analogy of a train of gunpowder, which I have used before, there is no doubt that propagation occurs primarily because each layer that has begun burning heats up the next layer, and causes it to burn too. In the case of phosphorus this explanation is hardly tenable, because the phosphorus vapour present is only a very small fraction of the atmosphere in which it is contained, and it can be calculated that it cannot yield enough heat to raise the temperature more than a degree or two, which would not be enough.

We must look for some other way in which the action in one layer can help the action in the next one; and the suggestion I make is that the action is of the kind called catalytic. The products of

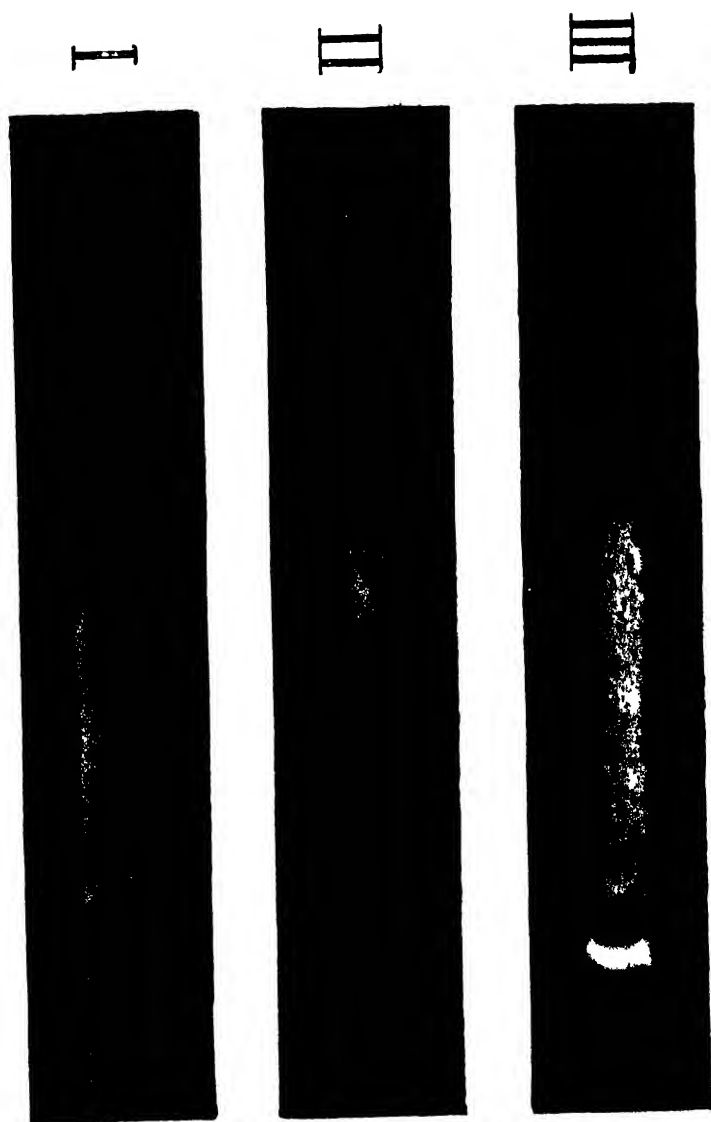


FIG 4A

IV



V

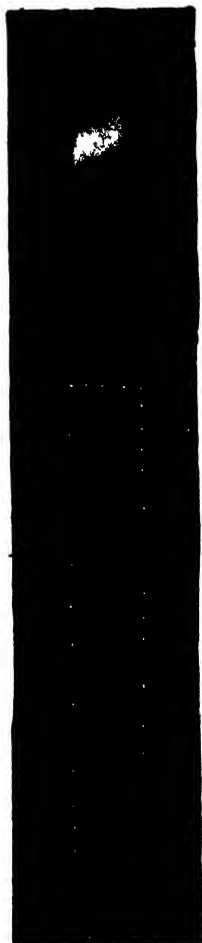


FIG 4r

combustion from one layer are able to promote the action in the next layer by a method analogous, e.g., to that by which finely divided platinum is able to promote so many chemical actions between gases, some of them of industrial importance. It is true that this explanation is incomplete and in a measure speculative. On the other hand, as I hope to convince you, it covers many facts otherwise very hard to co-ordinate: and if anyone is inclined to object to it, the most helpful thing he can do is to make his objection definite by calling attention to facts which are inconsistent with it, if there are any.

One of the most striking peculiarities of the kind of action I have referred to is the facility with which the catalyst is put out of order, or *poisoned* as the phrase goes. Several important industrial triumphs have depended on success in preventing this from happening. The exact condition of a surface capable of producing this effect is a very critical thing, and I believe that when the glow of phosphorus is inhibited, it simply means that the particles of phosphoric oxide, or other product of combustion, are spoilt, or *poisoned* by the condensation of molecules of the inhibiting substances upon them; and that this prevents them from assisting the propagation. It is noteworthy that most of the inhibiting substances are easily condensable vapours, such as would be likely enough to act in this way. Oxygen is an exception, but it must be noticed, first, that oxygen will only act when moist; and, secondly, it has to be present in enormous excess—about 20,000 molecules of oxygen for one of phosphorus vapour—before it can quench the glow. Inhibitors like ammonia doubtless act by definite chemical union with phosphoric oxide.

Lastly, the view I have explained requires us to suppose that the combination is always breaking out sporadically at isolated centres, though in the presence of an inhibitor it fails to propagate itself.

I have recently been able to prove directly that this does in fact happen when oxygen is the inhibitor. When the gas-pressure was lowered the phosphorus glowed: but when it was raised again the phosphorus went out abruptly, like a candle blown out. Nevertheless, under the latter condition, it was found by observations lasting over several weeks, that a slow absorption was going on all the time, and it was found that this action occurred between oxygen and the *vapour* of phosphorus.

This whole research has been rather off the main stream of scientific enquiry at the present time; but I hope it has convinced you that there is still a fascinating field for research about phenomena which have been familiar for centuries.

[R.]

Friday, January 16, 1925.

SIR JAMES CRICHTON-BROWNE, J.P. M.D. LL.D. D.Sc. F.R.S.,  
Treasurer and Vice-President, in the Chair.

SIR WILLIAM BRAGG, K.B.E. D.Sc. F.R.S. M.R.I.,  
Fullerian Professor of Chemistry.

The Investigation of the Properties of Thin Films by  
Means of X-rays.

THERE are a number of problems of the highest importance which are, or can be, contained in the study of what we call the "thin film." They are linked together by the fact that most reactions between bodies are largely determined by what takes place at their points of contact, and therefore by the nature of their surfaces. What is to be found in the interior of the body is often of much less importance than the composition and state of its surface film. The immensely varied problems of surface tension are examples of one kind: the phenomena of catalysis, of friction and lubrication are examples of other kinds.

Though the thickness of the surface film is so important, it is often very small beyond the limits of direct optical measurement. The X-rays measure more minute quantities than the microscope, and we may well ask if they carry us any further. They measure only, it is true, the spacing of a stratification, and a stratification cannot consist of a single layer or film: so that the rays cannot be applied directly to the examination, for example, of the black spot on a soap film. But they are able to help in an indirect yet effective way. For they deal with problems of the arrangement of molecules, and all these manifestations of surface action are directly dependent on the arrangement of the surface atoms and molecules. Also the substances, the actions of which in single thin films are of great interest, are often found multiplied into crystals which actually can be examined by the X-rays.

The soap bubble and soap film have long been studied for their beauty and their interest. Since they have so large a surface in comparison with their volume content, they offer special advantages for the examination of surface actions. Yet they are so full of detail that even within the last few years new and most interesting discoveries have been made with respect to them. It will be convenient

to review some of these briefly as illustrations of the facts that have to be accounted for.

When the bubble is near its end a black patch often appears, and soon afterwards the bubble bursts. The patch is black because it is so thin, and therefore reflects little light. It might be thought that the "black spot" represents a breakdown in the structure, a forerunner of collapse. But it is in reality a relatively stable affair: in proper circumstances it can be maintained for hours and days, as Sir James Dewar loved to show. Reinold and Rucker, Rayleigh, Johannot, and many others were greatly interested in the sharpness of its outline, its thinness, and the uniformity of its texture. They recognised two degrees of blackness, as Newton had done long before; they supposed them to represent a single film and its duplication. They succeeded in measuring the thickness, and estimated it to be about 60 Ångström units in the case of the thinner, and twice as much in that of the thicker.

When a film is correctly prepared and mounted, the black spot appears at once at the top of the film, a horizontal line separating it sharply from the rest with its horizontal bands of colour. Small black spots are continually forming at various points of the coloured film, and rushing up to join the main spot: it is, of course, the downward movement of their surroundings which makes them move in the opposite direction. Sometimes minute points of light like stars appear, moving about on the surface, and especially at the edges of the black spots—drops of water apparently.

When observations of this kind are made in the quiet of a laboratory, with small and more manageable films, and with special instrumental facilities, a fineness of detail is revealed which cannot be followed on the screen. Our knowledge of these details is due to the beautiful work of Perrin, published in 1918, and to its repetition by Wells in 1920. To state Perrin's results very briefly, it appears that the two degrees of thickness first observed are due to the existence of a very thin uniform film and its doubling, as had already been shown; that the existence of three more degrees of blackness observed by Johannot was due to further repetitions of the same layer, and that a close examination revealed the existence of dozens of these layers, all multiples of the same fundamental thickness. In the blackest spot there was but one layer, and this was, strangely enough, the most stable of all. Other similar layers could be found superadded, like sheets of paper of the same uniform thickness, until the film was thick enough to show the rich colours of Newton's rings which the soap film ordinarily displays. As we know, the colour of the film is an indication of its thickness. For example, the colours proceed from black through greys, becoming lighter and lighter as the thickness increases, then to a nearly pure white, then through straw-yellow, yellow, orange-red, dark red to a violet, which always changes very quickly with alteration of thickness, and so

forms a definite stage. The thickness has now reached (for water) about 2100 Å. Perrin counted 37 to 38 steps by which the superimposed sheets mounted to the full thickness that gave the violet tint. He made measurements also with chromatic light, and as his final result arrived at the conclusion that the thickness of the single film was about 52 Å. Wells found a somewhat smaller value, namely, 42 Å. Perrin, and Wells after him, concluded, on evidence which we have not time to consider, that the single film was composed of a double layer of oleic acid, arising from the hydrolysis of the sodium or potassium oleate in solution.

Now, Rayleigh, Devaux, and more lately, Langmuir, Hardy and Adam have measured the thickness of an oil film spread on the surface of water. It appears that in the case of a fatty acid such as stearic or palmitic, when the surface is fully charged, the long chains stand on end, their carboxyl terminals rooted in the water, for which they have a great attraction, and their methyl terminals all turned outwards. The length of the oleic acid molecule is about 23 Å. It is clear that this length can easily be in agreement with the suggestion made by Perrin. His film of 52 Å., or 42 Å., according to Wells, would consist of two layers of oleic acid molecules, the carboxyl ends meeting in the centre. The molecules are held together, side by side, to form a strong sheet, while the methyl groups form a surface reacting very slightly with anything outside.

The examination of crystal forms by means of X-rays shows that the peculiar arrangement of the molecules in these films on water extends also to the solid crystal in a great number of cases, and may probably be considered as characteristic of the structure of a large and important class of substances. It is in the first place to be found in the solid forms of the fatty acids, hydrocarbons, alcohols, and other long-chain molecules. These have been examined by Piper at Bristol, and by Muller and Shearer in the Davy Faraday Laboratory. I referred to a few of these a year ago. The number examined has been largely increased during the last twelve months, and the results that have been obtained are ready for publication.

When a small quantity of one of these substances is placed upon a plate of glass or mica, either by melting or by pressing, a formation of layers results, much more so by the latter operation, for it would appear that the pressing and working encourage the arrangement of the molecules and the regularity of the layers that are formed. The material is now placed on an X-ray spectrometer, and a photograph is taken by the method of the revolving crystal. The photographic plate shows usually a number of lines which clearly represent the orders obtained by reflection from the plane of the layers. In this way the thickness of the layer can easily be measured with an accuracy of about 1 per cent. Ten or more



orders are often observed. The cleavage plane of many crystals, especially of the class I am describing, often gives several orders, but not usually so many as in this case: other reflecting planes may give only one, perhaps two, higher orders of moderate strength, more often only very weak reflections, except in the first order. No doubt the case is parallel to the well-known effect in optics, where a grating yields many orders of spectra when the lines are sharp and fine. The "line" in this case is a well-defined discontinuity in the distribution of scattering centres which occurs at the ends of the long molecules; a defect would be caused by the presence of the hydrogens of a methyl group, an excess by the oxygens of a carboxyl group. We may suppose the planes which separate layers of these molecules to be well marked in this way, and that otherwise there is a fairly even distribution along the body of the molecule.

If we plot the spacing of each substance of any one series against the number of carbon atoms in the chain, we find at once that the indicating points lie exactly on a straight line, except when the chain is short. This has been proved by Muller and Shearer for the fatty acids, hydrocarbons, alcohols, ketones, and in other cases, and the regularity of the results leaves no doubt as to facts. The increase for each carbon atom is either about  $1.0 \text{ \AA.}$  or  $1.3 \text{ \AA.}$ , the former occurring in the fatty acids, for example, and the latter in their esters.

If we may assume that the molecules lie perpendicularly to the layer, the numbers found for the thicknesses are actually the lengths of the molecules, and there is some ground for supposing this to be often true. But, of course, the molecules might *not* be normal to the layer, in which case the length of the molecule would be more than the thickness of the layer. It is certain that this may sometimes be so. Small crystals of substances of this class have been obtained and successfully measured in these laboratories by R. E. Gibbs, in spite of the fact that they each weighed only about a hundredth of a milligram. Gibbs finds that the crystals are of monoclinic prismatic form.

In this instance, then, the molecule is not upright, but sloping. It is difficult to imagine that the molecules all slope one way in the oil films on water; there would surely be some unique and recognisable direction in the film. It is possible that the explanation may be found in the fact that there are actually two ways, perhaps several ways, in which the molecules arrange themselves. Gibbs has found an orthorhombic as well as a monoclinic form; and Muller has observed that a hydrocarbon gives a somewhat different value for the spacing when it is only a few degrees below its melting-point. The physical appearance is different in the two cases. In the latter the film is translucent: in the usual case it is opaque, probably on account of minute crevasses formed during shrinking. This may be the cause of the change we see passing over cooling candle grease: it is transparent one moment, and suddenly clouds over.

The inclination of the molecule to the plane of cleavage must be finally settled before we are quite sure that we are measuring the actual lengths of the molecules, but we may hope for an early solution.

The fatty acid molecules are in double layers, but the hydrocarbons are not. We know this in two ways. In the first place, the actual increase in length for each carbon atom is twice as great in one case as in the other. In the second place, the even orders of the fatty acid spectra are very weak compared to the odd orders.

Such an effect can be produced in an optical grating by an alternation of white and black lines on a grey ground. An alternation of strong and weak black lines gives strength to the even orders. The substitution of white for one of the blacks is equivalent to changing the sign of its contribution, and the strength passes over from the even orders to the odd. Gratings can be so made as to illustrate the point. If molecules pointing opposite ways are joined by their carboxyl terminations, then the methyl ends of the molecules are weaker in scattering centres than the general average along the molecule, but the parts where the carboxyl groups join together are above the average in strength.

Shearer finds another illustration of this effect in the case of hydrocarbons which form a single layer, but are converted into ketones by the substitution of oxygen for hydrogen at some point of the length. When the substitution is at the middle of the chain, there is at that point an excessive number of scattering centres, and we have again the circumstances that cause reinforcement of the odd orders. But if the substitution is not at the middle of the chain, the odd orders are no longer strong compared to the even.

We have, therefore, in these stratified layers which we are examining by the X-rays, the very same formation that Perrin has observed in the liquid films. The molecules are found, without exception, to be extended to their full length, and linked together by their carboxyl terminals. Shearer finds the length of the double molecule of oleic acid to be about 36, which is to be compared with the 52 of Perrin and the 42 of Wells.

The conditions which lead to the formation of films on a water surface, and layers in the fatty acids and similar bodies, are operative also in the case of a large number of more solid crystals. A certain flakiness is the result, the crystals cleaving very easily into thin layers which slide readily on one another, and often give a greasy feeling to the crystal.

Naphthalene and anthracene are cases in point. Their molecules are long and narrow, and are arranged side by side like the oleic acid molecules on water. A single layer is like the corn in a field; but they lean over like the corn when a wind is blowing. They are not perpendicular to the layer. The bonds that tie the molecules side to side must be stronger than those that tie them end to end, because the flakes are so easily parted from one another. The

naphthalene molecule contains two hexagonal rings of carbon atoms, and the anthracene molecule is extended by the addition of a third, so that the layer is thicker in the latter case. In both cases the molecule has a centre of symmetry, and in each layer the molecules are divided into two classes in respect to their orientation. Any member of one class is joined up by ties of some sort to several (probably four) members of the other class, which immediately surround it in the flake; and it would seem that this cross linking holds the flake together and gives it its strength.

It is likely that a very large number of other substances are built on the same plan. Even when their examination has not yet been attempted by means of X-rays, their crystallographic measurements suggest the fact.

In other substances a similar external form is attained by a somewhat more complicated internal arrangement. The molecule has of itself no centre of symmetry, in fact no symmetry at all, and twice as many are required in the construction of the monoclinic prismatic unit of pattern. This is the case, for example, with benzoic acid, and probably with many of its derivatives. But there is the same flakiness which may be put down to the same causes: (1) the general orientation of the molecules so as to lie across the flake, and (2) the hydrogen terminations. In all these cases we find that the crystal is tied together by links extended from each molecule to neighbours of the other possible orientations; this seems to be an essential feature of crystal construction. It cannot, of course, be followed in the lowest type of crystalline symmetry, where there is but one orientation possible, and every molecule is arranged exactly as every other. But though this arrangement can be conceived, it is doubtful whether there is a known case: it has been shown by Astbury that calcium thiosulphate, generally quoted as the solitary example, has probably the symmetry of Class 2, which contains two orientations, connected by a centre of symmetry. Whether this is so or not, it is certain that in at least the vast majority of cases cross linking is an important feature. It may very likely be a factor in the determination of the faces that appear on a crystal. A face will naturally contain specimens of more than one molecular orientation, so that the elements of the face may be tied together strongly. For example, in naphthalene, as in many other cases, all the usual faces contain equal numbers of molecules of the two orientations; one might even predict the arrangement from the knowledge of the form.

If, therefore, we survey the general characteristics of this large class of flaky crystals, we observe that the monomolecular films of Langmuir and the multiple stratifications of Perrin, and the whole range of "thin films," have much in common with the solid members of the class. Yet there are significant differences. It seems possible by studying both resemblances and differences to obtain some fresh light on the properties of the more "liquid" films.

With these facts before us we may perhaps formulate a more detailed theory of the black spot on the soap film. The ordinary thick film is bounded on each side by the monomolecular film of oleic acid. In this film there is certainly arrangement. Adam, in particular, has examined the compression of the film under applied forces, and his observations and conclusions fall in naturally with the ordered array that we should expect to be there. But the film is imperfectly crystalline. It is compressible up to a certain point, and during the range of compression may be considered as a two-dimensional gas. The perfect crystal of this class of substance is found in the films studied by Muller and Shearer, and in the minute crystal which Gibbs has measured. The perfect crystal of oleic acid contains twice as many orientations as the film of oleic acid on water: the molecules on the water are only one way up, and the reversed molecules are required to complete the structure.

Suppose, however, that the oleic acid films on the two sides come into contact anywhere; the conditions for the completion of the crystalline structure are now all present. The carboxyl groups not only meet, but interlace: each molecule in the upper group linking together two or four molecules in the lower, and vice versa. This is doubtless a far more stable form of arrangement than that of the single film. The two outside single films, once united in one place, must increase their area of contact, and will drive the expelled water before them until the accumulating heap becomes too great for them to push any further, the action being assisted by the tension of the rest of the film.

The film thus formed is a real crystal, because it contains all the molecular orientations. The black spot is simply the thinnest possible flake of oleic acid. It is true that oleic acid melts at  $11^{\circ}\text{C}$ ., but the crystalline structure is there, in a mobile state. Solution cannot be made to enter between the two surfaces now united in crystalline fashion. Other films may be formed and float about on it, holding on by virtue of the feeble attractions of the methyl groups on one another: even the pressure of the air must help in keeping them together. These added films will slide about easily; they also will be true crystals of oleic acid, probably without any water.

The differences between the conditions and structure of the black spot on one hand and the neighbouring thick film on the other are so great that we may cease to wonder at the sharpness of the boundary and the enormous change in thickness; on one side of the boundary the thickness may be hundreds of times as great as on the other.

When the black spots appear and rise through the thick part of the film to join the general black area at the top, they leave trails behind them; they look like tadpoles swimming up to the top of the water. When the motion becomes less violent the tails shrink into small circular spots. On the other hand, if a thick patch is forced

by the general turmoil into the middle of a black film, it tends also to a circular shape.

We come now to another of the important surface effects, namely, that of friction, or, stated inversely, of slipperiness. These flaky substances are in general slippery and greasy to the touch. The greasy feeling seems to be due to the ease with which the flakes are split from the main body of the substance, and then slide over it. Graphite is an extreme example of the flaky state; and without forcing its inclusion in the class of substances we are considering, we observe that the atoms in each flake are tightly tied together, and that there is a very weak linkage between a flake and its neighbours. It is the combination of these conditions that makes for good lubricating qualities. Now in these substances the same conditions hold to a greater or less extent; the molecules of stearic acid, for example, are tied together more tightly side to side than across the ends at which the methyl groups are attached. If, therefore, stratification exists to any considerable degree, the same consequences follow as in the case of graphite. In general, stratification is incomplete, which is another way of saying that a large perfect crystal of stearic acid is never seen. Pressure is one agent that causes stratification, so that if one presses a piece of stearic acid or other material, the very pressure produces the conditions for easy slipping. I have already mentioned that Shearer and Muller have often found that a portion of the material melted on to a piece of mica or glass, and placed on the spectrometer in the necessary position for giving reflections from planes parallel to the glass, was comparatively ineffective in this respect. It would give clear evidence of those two spacings which are found on all the plates, and are ascribed to the widths of the molecules and are independent of their lengths. When the specimen was pressed, or rubbed down on to the plate, the stratification spacing appeared at once, and the others disappeared, thus showing the nature of the rearrangement that had taken place. It may be that this effect explains other properties of greases. I am told that the special grease used in binocular fittings is made serviceable by working with a palette knife.

We must recognise, however, that the layers built into the crystal are not at all times ready to slide, otherwise a mere tilt of the crystal would cause them all to slide off one another like a pack of cards. There is a sticking friction to be overcome, exactly as in graphite. It is only possible to speculate as to the cause; perhaps it is a real molecular effect, and sliding only occurs when the bonds, weak as they are, are further weakened, as if the substance was about to melt; perhaps it is rather a mass effect and due to imperfect crystallisation.

It seems not unlikely that, at its best, slipperiness in these cases is almost perfect. Between two perfectly formed methyl layers there is very little friction indeed, perhaps none at all. The methyl layer

is seen at its best on the surface of the black spot in the soap film, and various writers have noted that one layer slides very easily over the other. Perrin, in fact, has directed attention to this remarkable effect, as shown in the Brownian movement of fragments of one layer, lying on and sliding over another.

In some of the experiments of Sir William Hardy and Miss Doubleday the condition of nearly complete slipperiness is attained. Their beautiful researches on "boundary lubrication," that is to say, the slipperiness of very thin films, have established certain rules of surprising simplicity. They have found cases in which friction nearly vanishes, and in general accordance with the above, they frequently occur when a solid lubricant is practically wiped and rubbed off the surface, a true stratification in a very thin film being probably left.

Not only the phenomena of surface tension and of lubrication, but also those of catalysis, must be intimately connected with the actual arrangement of molecules. We speak of stereochemistry as showing the relations of the atoms in the molecules to one another, their mutual orientation and distances. To deal with these subjects we shall have to extend stereochemistry to cover the mutual distances and orientations of molecules as well as of atoms. We see that we must not treat a molecule as if it were simply a sphere attracting according to gravitational laws; it is not even sufficient to speak of an atom in this way, except as an approximation in the case of ionic substances like rock-salt. If some super-Brobdingnagian enquirer were to argue from effects observed on the surface of the earth as to the nature of the human beings to which the effects were ascribed, and being unable to detect a single individual by the most refined methods of which he was capable, should say, "Let us provisionally assume the human being to be a sphere, having similar properties in all directions and no special points of attraction," he would not get very far towards a satisfactory explanation of his subject. It would be an advance should he recognise the existence of two types of opposite sign, and lay the foundations of an ionic theory of heteropolar assemblages, but even then he would fall far short of the truth. In the same way, when we try to explain surface tension as the result of the mutual gravitational attraction of spherical atoms or molecules, we cannot make much progress. Indeed, we sometimes arrive at consequences that appear startling, as when we determine their attractions by measuring the energy required to tear surface molecules away in the process of evaporation, and then proceed to deduce the existence of pressures of thousands of atmospheres within the body of a liquid. So we may measure the force required to tear away the fringing links of a piece of chain mail, take them to be due to mutual attraction between the links, and then deduce the existence of an enormous pressure within the piece.

It is when we consider a catalytic surface as possessing active

centres on its surface, the relative positions, magnitudes, and mutual distances of which are such that two wandering molecules of different kind, attracted by these points, may be held together, in a special way, that we get some idea of the fundamental action of catalysis. It is important to consider, as the basis of surface actions, the arrangements of the molecules at a surface, both arrangements that actually exist, and those that are predisposed to exist. This idea runs through all the work of those experimenters, Langmuir, Harkins, Hardy, Adam, Perrin, and many others who have made such progress of recent years; the X-ray studies emphasise this view, and supply many quantitative measurements by which it may be shaped and strengthened.

[W. H. B.]

Friday, February 27, 1925.

THE HON. SIR CHARLES A. PARSONS, K.C.B. J.P. Sc.D. LL.D.  
D.Sc F.R.S., Manager and Vice-President, in the Chair.

SIR JAMES C. IRVINE, C.B.E. LL.D. D.Sc. F.R.S.,  
Principal and Vice-Chancellor, University of St. Andrews.

### Sugars from the Standpoint of the Organic Chemist.

IF statistics are to be believed, the English-speaking races stand at the head of the sugar-consuming nations, and this, in itself, justifies us in devoting our attention to the scientific problems involved in these fascinating substances. There is an active and widely-spread interest in sugars, but the expression is comprehensive, including as it does a large variety of compounds, and no two individuals regard these substances in the same way.

Sugars, viewed from the standpoint of the man in the street, or of the cook in the kitchen, bear a very different aspect from the same substances when they engross the attention of the physiologist. The word "sugar," sounding in the ear of the economist, calls to recollection the refineries and their balance-sheets, but the imagination of the chemist is more profoundly stirred. To him, sugars and carbohydrates are not merely components of normal or luxurious diet, still less are they articles of commerce, or the basis of a national industry. He need not ignore any of these factors, but to him the sugars are essentially *molecules*, each with its definite structure, each possessing an individuality which enables it to react, transform or reform, within us and around us. The product of nature, as opposed to artificial, synthesis, the sugars form part of that great molecular channel through which solar energy flows to us.

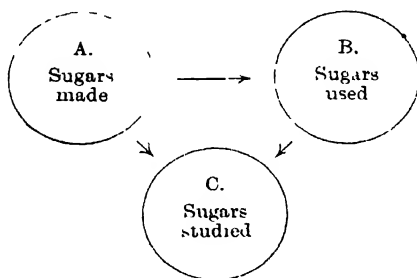
To-day we are passing through a scientific phase in which, after being dissected with the finest of physical scalpels, the molecule is regarded somewhat critically. Even the atom is not entirely safe, and it therefore requires a certain amount of courage to ask you to consider those complex curving chains of carbon atoms with their associated groups which the chemist formulates to represent the sugar molecules. Though courage be required, no apology is needed to



discuss here such complex problems of organic chemistry, for we are within a few months of the one-hundredth birthday of benzene, and are assembled at its birthplace. Also, the chemist is unlikely to forget that the theories of molecular structure, elaborated with patience and zeal in the course of the intervening century, are now finding fresh justification in the brilliant researches conducted within these walls.

I have said that the organic chemist views the sugars as molecules, but would add the further statement that his vision must be more than abstract. From day to day he studies reactions of carbohydrates in the flask, or turns to instruments of precision to determine their physical constants, but his mind must ever wander from the laboratory of stone and lime to those other laboratories of living cells, where Nature builds up and elaborates the sugars, or consumes them in the fire of metabolism. It is a difficult task to correlate the results of any one of these laboratories with those of the others, doubly so as the chemist, with lavish supplies of energy at his command, cannot compete in sugar synthesis with the humblest of the chlorophyllous plants, but it is a task well worthy of his endeavour.

In order to make my meaning clear, I may represent by a diagram the three types of sugar laboratory and the range of the chemist's interest:



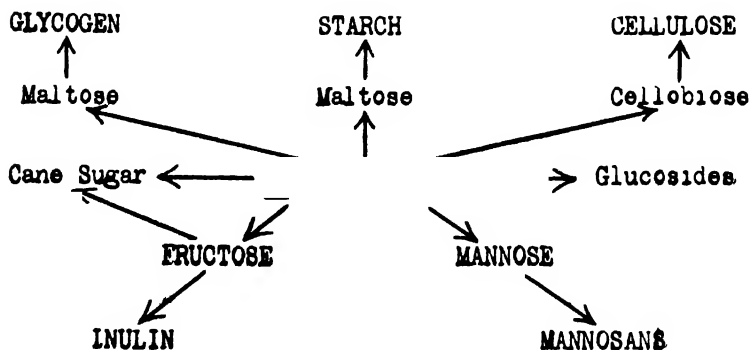
In plant life, represented by A., the sugars are formed, and in B., which symbolises animal life, they are utilised. In C., the chemical or physiological laboratory, the compounds are studied, while the investigator, working in C., and himself part of B., must watch events in all directions. So much for the human investigator and his task; we now turn to review what he has accomplished.

I shall not attempt in this lecture to trace the steps which have led to our present ideas of sugar molecules. It will be sufficient to say that, within the past fifty years, a veritable chaos has been resolved into something approaching order. Many new sugars have

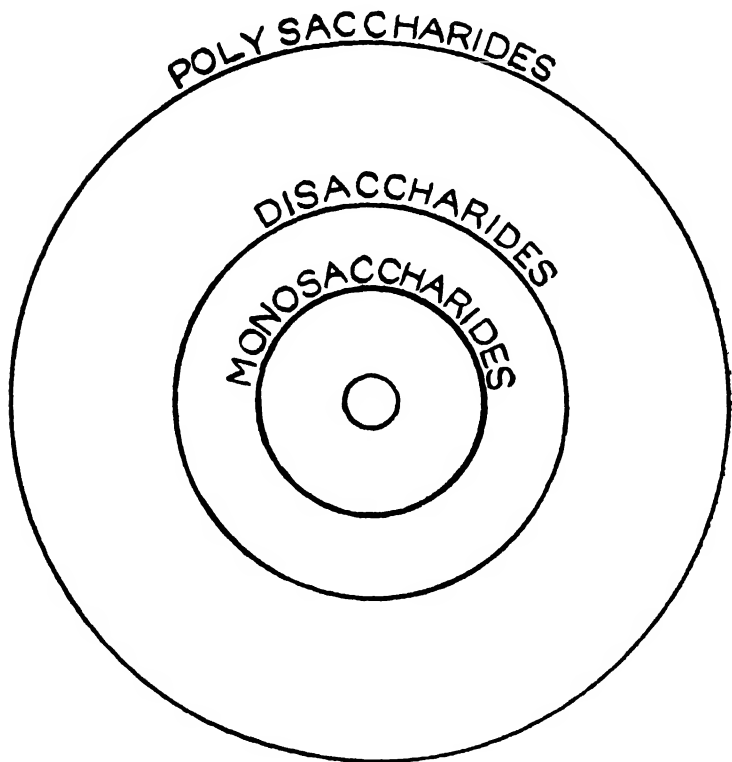
been isolated from natural sources, others, unknown in nature, have been prepared synthetically; formulæ have been ascribed to them, and in many cases the structure has been determined. As a result of these advances, carbohydrates may be classified roughly into the three great groups known respectively as:

I. Polysaccharides	$(C_6H_{10}O_5)_x$	Ex. Cellulose Starch Glycogen
II. Disaccharides	$C_{12}H_{22}O_{11}$	Ex. Cane Sugar Maltose
III. Monosaccharides	$C_6H_{12}O_6$	Ex. Glucose

This is not to be regarded as an exhaustive classification, but it will suffice to enable us to trace the essential relationship between the most important representatives. It will be observed that I have inverted the usual order and have commenced with the complex polysaccharides, for this reason, that they are essentially the starting point of the chemist's labours. From them, the simpler disaccharides can, as a rule, be prepared by hydrolysis, and by an extension of this process the monosaccharides are obtained. The classification, therefore, indicates the steps by which the chemist passes from the polysaccharides to sugars proper, but this does not imply that nature, through the agency of the living plant, follows the same path. The reverse, in fact, is generally the case, for although the chemist has achieved but little success in converting monosaccharides into disaccharides, and none whatsoever in synthesising polysaccharides, these operations are essential processes in plant life. I may, in illustration, represent the natural elaboration of carbohydrates by means of a chart based on a scheme recently suggested by Professor J. H. Priestley.

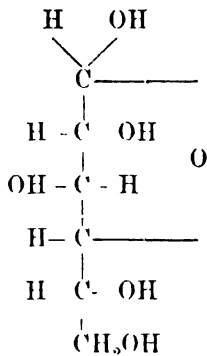


Here the simple hexose sugars are shown to be the source of the disaccharides, and these, in turn, lead to the polysaccharides. In a simpler manner, the same idea is conveyed by three concentric circles, representing respectively : Mono-, Di-, and Polysaccharides.



In the centre, the focus of importance and interest, lies glucose, the compound which I believe to be the origin of all the others. The circles may also convey the further impression of the ever-increasing difficulties which surround the study of these compounds, and of our decreasing knowledge regarding them, the further we go from the point of origin. The molecule of glucose is illuminated by much systematic research, those of the disaccharides are, one by one, becoming clearly discernible, while the mass complexes of the polysaccharides, if more shadowy, are gradually emerging from the

gloom. I am speaking, of course, in terms of our knowledge of molecular structure, for, until we have a clear view of how the various atoms are mutually linked together, we are limited to purely descriptive study of the compounds or compelled to experiment at random. Turning to the fundamental case of glucose, we find that the properties, so far as they are known, are satisfied by the structural formula—

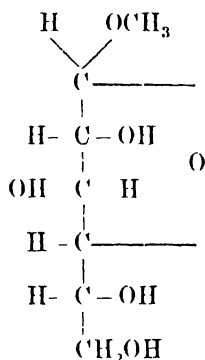


Now there is a natural tendency to regard the reactions of glucose as if the molecule as a whole were taking part in the changes, but so long as this restriction limits our attitude and we ignore the fact that there are five hydroxyl groups, each with its own specific properties, we shall never be in a position to interpret the subtle part played by this sugar in Nature. The essential reactions of glucose are attributable to the five hydroxyl groups, and these show a differentiation into three distinct categories :

- (1) the terminal  $\text{---CHOH}$  which is responsible for the reducing properties,
- (2) the hydroxyl groups within the ring,
- (3) the  $\text{---CHOH}\cdot\text{CH}_2\text{OH}$  fragment external to the ring.

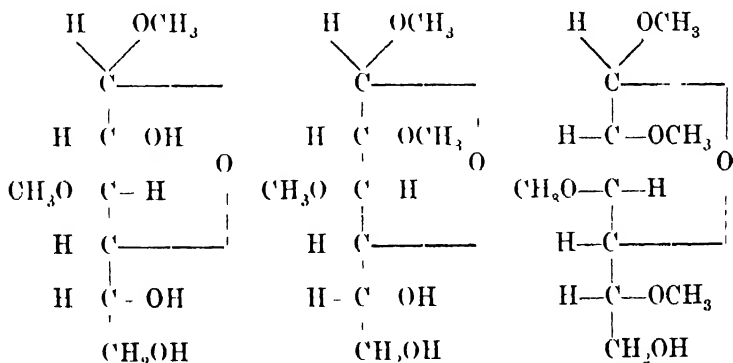
It is necessary, then, to study separately the individual hydroxyl groups of glucose ; but the question at once arises, How is it to be done ? One group is at once stamped as unique, and this is the terminal secondary alcohol group, which is responsible for reducing properties, but otherwise most reagents which effect these groups fail to discriminate between them, and it is impossible to arrest or control the changes once they have started. For this reason the special properties of the five hydroxyl positions have remained until recently unknown, but we are now in a position to place, as it were, a label on each group and observe how each behaves. How this is secured is easy to explain, if difficult to effect.

The hydrogen atoms of the hydroxyl groups can be replaced by methyl groups. This substitution has the effect of neutralising the reactivity of selected positions, putting them out of action, whilst leaving the remaining hydroxyl positions free to exercise their individual functions. As the simplest and most accessible example of these "methylated sugars" we have the compound known as methylglucoside, in which, as expressed in the accompanying formula, the reducing section of glucose is masked :

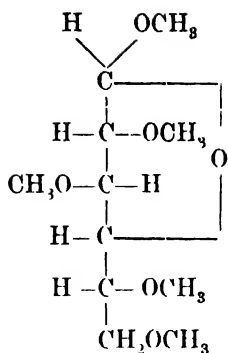


Many other methylated glucoses are known, and a few typical examples may be formulated in order to illustrate the variety of such compounds now available.

#### I. Non-Reducing Methylated Glucoses :

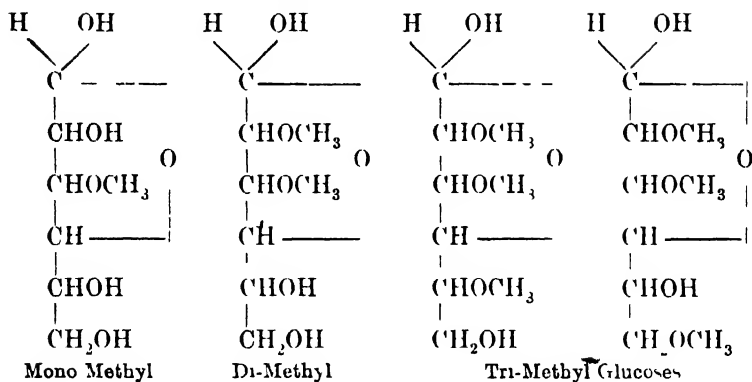


Finally, the limiting case is reached where no free hydroxyl groups remain, and where consequently all characteristic sugar reactions vanish.

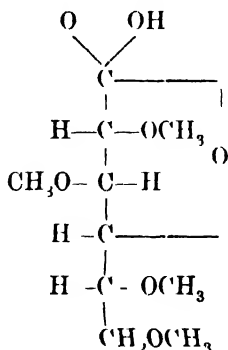


Pentamethyl glucose

## II. Reducing Methylated Glucoses :



In this particular instance, the limiting case is reached with tetra methyl glucose :



2 3 5,6-Tetramethyl Glucose

where only the reducing group is operative and all other positions have been rendered non-reactive.

The preparation of even a few grams of these sugars is, in most cases, possible only after many months of laborious work, and, consequently, it is impossible to demonstrate their formation on the lecture table. I may, however, illustrate by means of models the manner in which the sugar molecule may be manipulated so as to obtain some particular derivative, and select for this purpose the case of dimethyl glucose. The practical steps arranged in order are :—

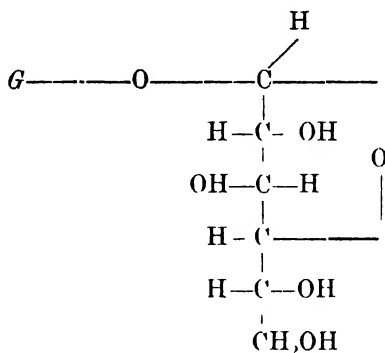
- I. Preparation of the Methylglucoside.  
↓
- II. Condensation of the product with Benzaldehyde.  
↓
- III. Methylation.  
↓
- IV. Mild Hydrolysis.  
↓
- V. Complete Hydrolysis.

Reactions I. and II. have as their object the temporary protection of three selected hydroxyl groups, while No. III. introduces methyl groups into the portions still left vacant. Then the earlier processes are reversed when the protecting groups are removed in the final stages. To use an analogy, a design is obtained by means of a stencil.

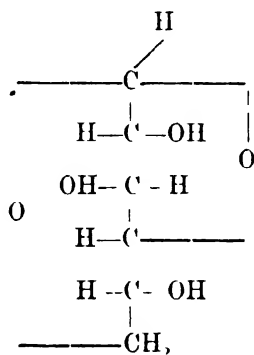
As is to be expected these methylated glucoses diverge more and more from the parent sugar as the number of methyl groups is increased, so much so that finally, in the higher examples, the compounds in place of being sweet have a burning taste like that of alcohol, and can be distilled readily in a high vacuum.

The study of these compounds has revealed a number of interesting features, one being that the fermentation of glucose to give alcohol is at once arrested if even a single hydroxyl group be substituted. Here, then, is a case where it can be claimed that the entire molecule is necessary before this important change can proceed. This is, however, exceptional, as undoubtedly the chief properties of glucose are attributable to three parts of the molecule. These are respectively the reducing group at one end of the carbon chain and the two hydroxyl groups at the opposite end. For convenience, and to indicate the carbon atoms to which they are attached, they may be indexed as 1, 5, and 6. Group No. 1 is the portion of the sugar most readily affected by oxidising media, and, indeed, is the most reactive part of the whole molecule. It is concerned in the formation of both the artificial and natural glucosides (including cane-sugar), which are

formed when glucose condenses with hydroxyl-compounds to give the general structure shown below :



Further, and this is an important point, the reducing group is involved when glucose is dehydrated and converted into  $\text{C}_6\text{H}_{10}\text{O}_5$ , which we may regard as the forerunner of the polysaccharides. Of these substances the best defined is the compound known as glucosan, which can be formulated as :

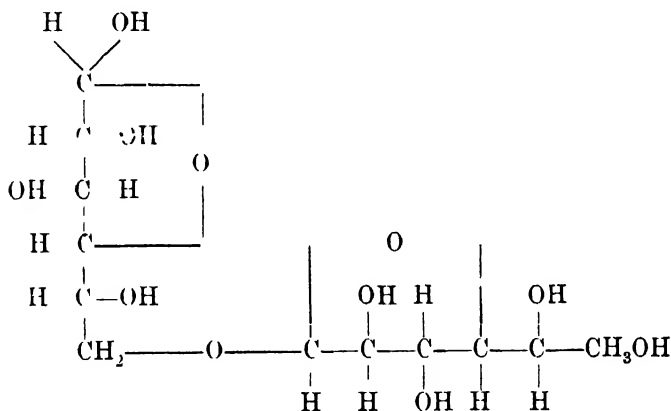


Again, the physiological potency of the reducing area of the glucose molecule is shown in innumerable ways, as it is through this position that nitrogen, or ketones, such as acetone, become attached to the sugar. Positions 5 and 6, if less reactive, are equally characteristic, either alone or in conjunction with No. 1. Thus dehydration takes place much more readily between 1 and 6, or 1 and 5, than with any other pair of hydroxyl groups, and, as a recent research has shown, the

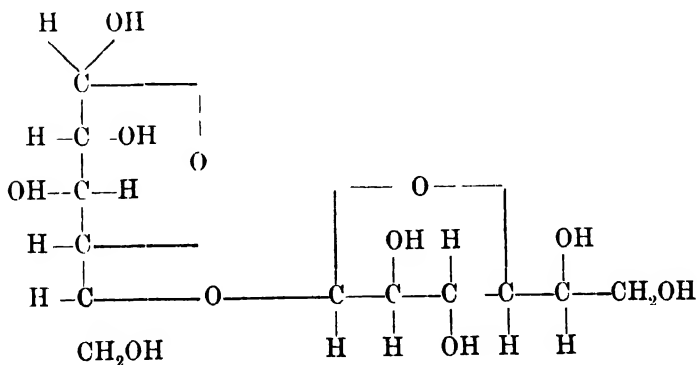


physiological effect of glucose in combating an over-dose of insulin vanishes when the hydroxyl group in positions 1 or 5 is substituted.

Taking now the specific properties of these terminal hydroxyls, it is clear that No. 6 is highly reactive, for it can be replaced or reduced, esterified or oxidised with a facility which is imperfectly recognised. It shares also the chief characteristic of No. 5 in the marked tendency to function as a point of attachment through which two glucose molecules become united to form reducing disaccharides. Taking the two examples presented by maltose and cellobiose, the union of the two hexoses takes effect in different positions, as shown by the formulæ :

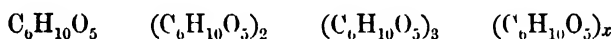


Maltose



Cellobiose

These views have been arrived at through the study of methylated sugars, and without committing myself to them as final, they represent the facts so far as known. Observe how each of the above sugars still retains highly reactive hydroxyl groups, thus indicating the possibility of further transformation. A disaccharide should be capable of condensing with other glucose molecules to give in succession tri- or tetra-saccharides, and the possibility is always open that a molecule of water may be lost with the subsequent formation of the corresponding anhydride. We can therefore postulate the existence of a series of compounds, all possessing the same empirical formula, but differing in molecular magnitude :

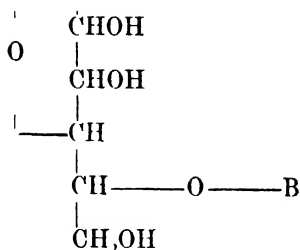


In other words, if we had not known of such polysaccharides as starch and cellulose, we could have used our present knowledge of the glucose molecule to predict the existence of these compounds, and could, in fact, have ascribed structural formulæ to them in advance.

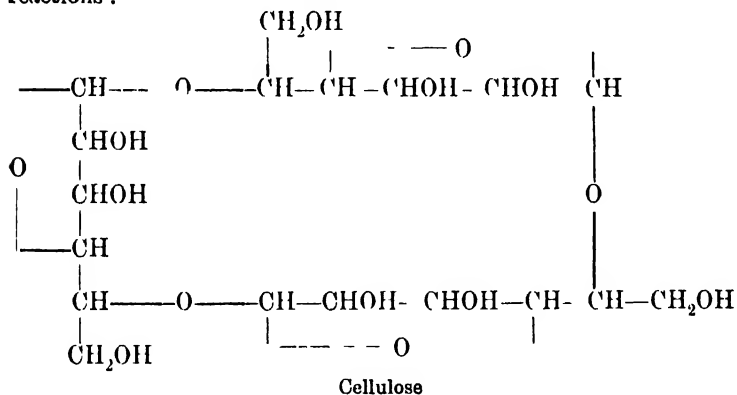
This brings us to the outer circle of the carbohydrates, and I wish to devote a short time to the consideration of at least one case of a polysaccharide. Taking cellulose as an example, it is evident at once that we have to deal with something which is far removed from the simple sugars. The great stability of cellulose, its insolubility and its capacity to form colloidal systems all point either to a molecule of large dimensions or, alternatively, to a highly polymerised aggregate of simple molecules. To fall back on analogy, cellulose may be compared to a wall in which the individual bricks may either be merely cemented together, and therefore detachable, or may have been fused together so as to form one large complete unit. Recent investigations have discredited the idea that cellulose consists of large molecules, so that, again falling back on analogy, the wall is now regarded as composed of relatively small bricks. The question at once arises : What is the shape and size of the individual bricks, and in what positions are they joined together ? Cellulose may be :

Anhydro-glucose	$(\text{C}_6\text{H}_{10}\text{O}_5)$	polymerised $n$ times.
Anhydro-diglucose	$(\text{C}_6\text{H}_{10}\text{O}_5)_2$	polymerised $n/2$ times.
Anhydro-triglucose	$(\text{C}_6\text{H}_{10}\text{O}_5)_3$	polymerised $n/3$ times.

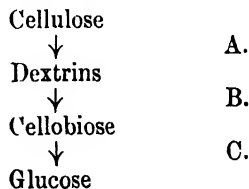
When cellulose is methylated, methyl groups enter only the hydroxyl positions of the molecule and a trimethyl cellulose is obtained. This, on hydrolysis, gives the corresponding trimethyl glucose and no other product. As the constitution of the sugar is known, we arrive at the conclusion that cellulose must contain the unit :



This structure may be completed by joining the valencies indexed as A and B, or may be extended by the introduction of similar units at A and B. The bulk of the chemical evidence favours the latter alternative, and the following structure is in best agreement with the reactions :

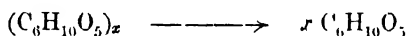


According to this view cellulose is anhydro-triglucose, polymerised to an unknown extent. The shape of our brick has been determined, but although its size remained a little doubtful, I am now in a position to submit additional confirmatory evidence. To explain how this has been done demands a review of the stages in which cellulose can be broken down to give glucose by the process known as "acetolysis." This is shown by the diagrammatic scheme :

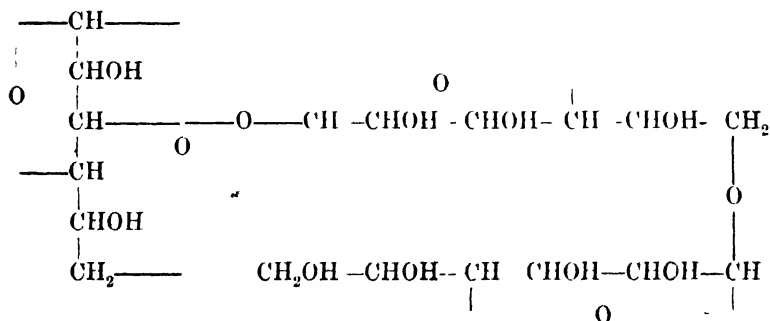


and clearly the hydrolysis reactions of B and C are preceded by depolymerisation at stage A. If then the reaction can be arrested before hydrolysis has become effective, we should have in possession the unit of cellulose. This has been accomplished, and an amorphous solid obtained which has been methylated so that it can be purified by distillation in a high vacuum. Analysis and molecular weight determinations agree accurately with the trisaccharide unit, which has now a mass of chemical evidence in its favour. But what are the forces which join these units into the large aggregate, and through what agency are they marshalled to form the cellulose fibre? Here the bewildered chemist turns for enlightenment to the physicist.

I have already deplored the inadequacy of the efforts made to conduct syntheses in the sugar group, and this naturally applies with greater force to the case of the polysaccharides. But I should like to lay before you briefly an account of another research, likewise unpublished, which shows how, almost by chance, the chemist has groped his way into a reaction which is closely akin to the synthesis of starch. Some years ago Pictet showed that starch when exposed to the drastic process of vacuum distillation is converted into glucosan, and he concluded from this result that simple depolymerisation had taken place :



Now glucosan resembles glucose in being definitely crystalline and freely soluble in water, but these properties disappear when the compound is fused with finely divided metals, a product being obtained which displays a close similarity with starch. The result can now be expanded. The polymerisation of glucosan proceeds most readily by heating with traces of metallic chlorides, giving a Tri-glucosan  $(\text{C}_6\text{H}_{10}\text{O}_5)_3$  and a Poly-glucosan  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ . In order to obtain the necessary analytical and structural evidence, triglucosan was methylated and distilled in a high vacuum. Molecular weight determinations showed that the product contained three glucosan units, and on hydrolysis three methylated glucoses were obtained in equal amount. These were respectively 2:5-dimethyl glucose, 2:3:5-trimethyl glucose, and 2:3:5:6-tetramethyl glucose, so that the constitution of the parent compound is :



This is a striking result, for the compound evidently contains the maltose structure which is characteristic of starch. Further the combined evidence supports the view that polyglucosan is based on an anhydro-trisaccharide unit, so that in this crude and drastic series of reactions the sugar residues have been made to arrange themselves as they do when starch is formed in the plant. I am willing to admit all criticism of the methods, but the result is a decided, and indeed the first, step towards the synthetical formation of the most important of the polysaccharides.

What I have described has been based largely on the molecular structure of sugars as displayed by their artificial reactions, and it is inevitable that the philosophic chemist should look forward and ask what are the future problems of the sugars and what developments are at this stage most desirable. If I may venture an opinion, it is that, for the time being, researches on constitution have nearly reached the limit of their efficiency, and have, in fact, outpaced efforts to study new reactions of the sugars themselves. Many problems which lie at the very foundation of sugar chemistry are still unsolved. What is the first sugar molecule formed in the plant, and from what simpler compounds does it arise? To what cause does the molecule owe its optical activity, and why is the glucose configuration favoured in preference to any other? What is the chemical process which operates so easily in Nature whereby glucose and fructose are interchangeable? How are the hexose molecules dehydrated, and in what manner are the products polymerised to the polysaccharides? These questions are but part of the great problem which has to be solved before we are in a position to interpret the reactions of the living plant; and how far we are from providing the answers!

It is not alone the fact that we have so much to discover which is disconcerting, for there comes also the chastening thought that possibly much of the chemist's work in the past has been conducted on wrong lines. All too frequently he uses powerful reagents or comparatively high temperatures, and, speaking generally, his methods are those which no plant could, or would, employ. Only those who have attempted a sugar synthesis in the laboratory can appreciate the sense of defeat which comes in comparing the paltry result of years of labour with the rapid, economical and abundant syntheses of Nature. To make further progress I believe we must enter on a new phase when only such reactions of the sugars will be studied as proceed under conditions approaching closely to those which obtain in living tissues: conditions which will not admit of the use of solvents or reagents inimicable to life, and in which the optical, electrical, and thermal factors will be rigidly controlled. Above all, we require new types of synthesis, and only when the chemist resolves to regard it as a crime to conduct a sugar reaction at the boiling-point is there any real hope for sugar chemistry.

I do not seek to disparage the past labours of the chemist, or to

minimise his achievement in establishing the views of structure which I have laid before you, but the worker in this field needs help. He needs help from all the sciences which surround and permeate chemistry. Eighty years ago Faraday was investigating the electrical properties of cane-sugar, and the recollection inspires the hope that the research now associated with this place may again be applied to the whole series of carbohydrates. What a prospect is opened up when we shall have acquired well-founded conceptions of constitution based on both physical and chemical evidence !

[J. C. I.]

Friday, March 20, 1925.

SIR EDWARD POLLOCK, F.R.C.S., Manager and Vice-President,  
in the Chair.

J. W. MCBAIN, D.Sc. F.R.S.,  
Professor of Physical Chemistry, University of Bristol.

### Soaps and the Theory of Colloids.

THE subject of colloids has suffered from an excess of conflicting speculations in the absence of precise and definite experimental evidence. It is still found difficult to devise methods of experiment which will yield results which are exact and also unambiguous.

At the time when we began work in this field one of the chief recognised characteristics of colloids was their changeability and the dependence of their behaviour upon the vagaries of individual specimens. Our object was thoroughly to study one typical colloid in order to supply the definite evidence required for testing or building up the theory of the subject. No general theory can be true which is incompatible with carefully-established experimental evidence obtained with any one typical material.

Our chief experience is that the more carefully the colloid is studied the less colloidal it is found to be.

Soap is a unique material for the investigation of colloidal phenomena, because it illustrates nearly all the behaviour found in other colloidal systems, and is one of the few common reversible colloids which have a definite, simple, known chemical formula. Last, and most important, all results with soap solutions are quantitatively reproducible, and, in the many cases where our results have been tested in other laboratories, the experimental data have always been confirmed. We have been able to find one precise relationship after another; so that the results are almost lifted out of the colloidal field. Nevertheless, it remains true that soaps are typical colloids, and that the results are of general significance in determining the behaviour of colloids and their relationship to other states.

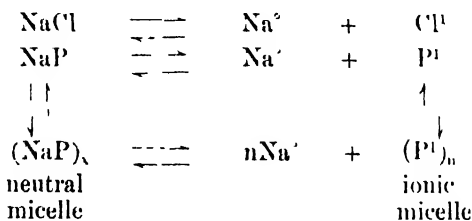
Soaps exhibit an apparently inexhaustible variety of behaviour, and few days pass without our making some new and interesting observation. A great deal of incidental information is obtained in our quest. For example, under certain conditions twice as much

soap is required for a given amount of detergent action if the soap solution is allowed to stand for a day before use. Again, Miss Laing has carried out analyses which show that the substance which accumulates in the surface of soap solutions and of soap films is not free fatty acid, but a mixture of acid sodium soap with neutral sodium soap, a very slight excess of alkalinity in the soap solution converting it all to neutral sodium or potassium soap.

Soap is important as a type of a great class of substances known as colloidal electrolytes. It is essential carefully to examine the evidence obtained by a study of ordinary solutions of soap, since from it follows directly a proof of the micellar theory. The essence of the micellar theory is that not the chemical molecules but aggregates of particles are the colloidal units.

It is necessary to show that hydrolysis, although always present to a slight extent, does not account for the major properties of the solutions. There are only traces of free fatty acid present, and there is but little free alkali, far less than in sodium carbonate; this has been shown by half-a-dozen independent quantitative methods. Hydrolysis is only of importance in dilute solutions. This is borne out by the fact that the hydrogen soap, cetyl sulphonic acid, has properties exactly parallel to ordinary soap in concentrated solution. Hence, the major properties of a strong soap solution are due to the soap itself.

We have found that in dilute solution soaps are ordinary crystalloids just like common salt, and dissociate into sodium and potassium ions and simple fatty ions. Upon concentrating the solutions, however, the undissociated soap molecules aggregate to form large particles of neutral soap—that is, neutral micelles. Likewise the fatty ions unite in small groups to form a new type of particle—the ionic micelle—in which there is one free charge for each fatty ion. By changing the concentration or the temperature all intermediate proportions of these constituents can be produced. This may be summarised in the following scheme:—



The evidence for the foregoing conception is based upon a study of osmotic effects and of electrical conductivity. The osmotic effects as exemplified by the lowering of freezing point, of dew point and of vapour pressure, and also the minimum pressure required for ultra-



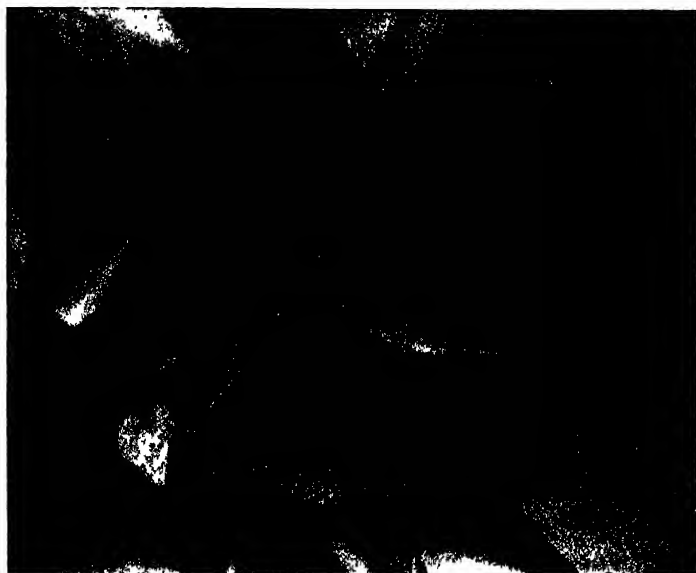


FIG. 2.  $-9.0 \text{ N}_v$  SOLUTION OF POTASSIUM LAURATE, IN LIQUID CRYSTAL-LINE CONDITION BETWEEN CROSSED NICOLS.

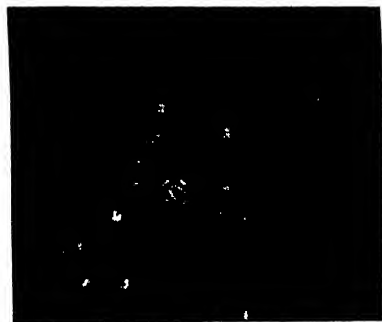


FIG. 1.—SUSPENDED DROPLETS OF LIQUID CRYSTAL = AMMONIUM OLEATE BETWEEN CROSSED NICOLS.

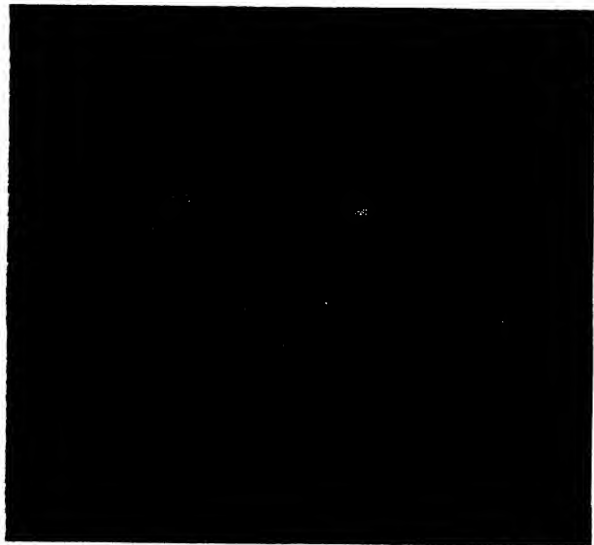


FIG. 3.—0.5 N<sub>w</sub> SODIUM LAURATE, CRYSTALLISED IN LAMELLAR FORM AT ROOM TEMPERATURE (Compare Fig 4)

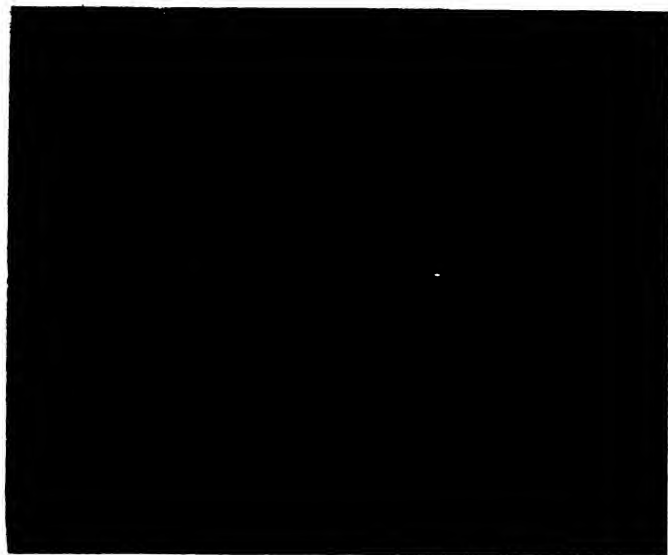


FIG 4.—0.5 N<sub>w</sub> SODIUM LAURATE, CRYSTALLISED IN CURD FORM AT ROOM TEMPERATURE. (Compare Fig. 3.)

filtration, are in general half of the values to be expected for the same concentrations of a typical salt such as sodium acetate. On the other hand, the conductivity of concentrated solutions is fully equal to that of sodium acetate. A large mass of data, obtained chiefly in the Bristol laboratories, have established both these truths.

If now the whole of the osmotic effect be taken as a measure of the sodium ions present, thus leaving no other crystalloidal constituent present, rather less than half of the observed conductivity is accounted for. The other half of the conductivity must be due to colloidal constituents, and one of these constituents must have the same number of negative charges as there are positive ions; this is the ionic micelle. The undissociated soap, too, must be in the form of aggregates or colloidal particles because of its negligible osmotic effect; this is the neutral micelle, and of the two it is the most important.

Long ago Selmi and Nageli emphasised that not the chemical molecules but larger aggregates were the colloidal units out of which all larger structures are made. Nageli in 1858 coined the word "micell" from *mica* (a crumb) in order to have a term with no pre-supposition of crystal or any other particular structure. Many years of study of starch convinced him that the micelles of which these granules are composed are essentially crystalline, and now the X-ray work of Debye and Scherrer and Sponsler has shown that this is correct for such colloids as gold sols and wood.

In the case of soaps there is no direct evidence of crystalline structure of the individual micelle, but Nageli would have approved of the name micelle for the ordered arrangements based upon conceptions of polarity which since 1912 have become fashionable. The particles of neutral micelle in soap are found to range from a few hundred to thousands of Ångström units in diameter depending upon the soap and the conditions. These neutral micelles may be visualised by borrowing and modifying a suggestion of S. E. Sheppard ("Nature," 1921, cviii, 73). Each particle is like a pair of military hair brushes, in which the bristles represent the hydrocarbon chains of the molecules arranged parallel to each other in sheets, two such layers being put together hydrocarbon to hydrocarbon. The two backs of the brushes on the outside represent the hydrate layer and the an-ionised electric double layer. A general survey of the facts with regard to the electrical double layers (Journ. Phys. Chem., 1924, xxviii, 706) has shown that only a minute fraction of such a surface can ionise—hence the name "neutral micelle." Such a micelle would owe its stability to its internal polar arrangement of the molecules and to the external heavy hydration of the sodium and carboxyl group. The explanation of the stability of colloidal particles should be extended to the discussion of suspensoid particles where it is usually ascribed to the free

electrical charges. The present conception would explain the stability by the hydration or solvation conditioned by even an undissociated double layer, and at its maximum in the neighbourhood of uncompensated electrical charges. The principle here involved is the commonplace that like dissolves like, and that a particle remains in solution when it is completely surrounded or coated with chemical groups similar to those of the solvent.

The ionic micelle is more novel and is essentially different. It may be visualised by borrowing and altering a suggestion put forward by Reychler in 1914 for particles of soap, and more recently by N. K. Adam. It resembles a group of, say, less than a dozen eels tied together by the tails, and pointing outwards in all directions from the common centre. Each eel is a fatty ion with the charged carboxyl group outwards. These carboxyl groups also are probably hydrated. Such an ionic micelle cannot grow large because the electrostatic repulsion would increase as the square of the electrical charges. The diameter of the ionic micelle as measured is only a few score Ångström units. Many experiments on migration in an electric field have shown that the ionic and neutral micelles exist and move quite independently of each other.

The conceptions put forward are a quantitative interpretation of the constitution of soap solutions, and are therefore open to many kinds of direct test. One of the most cogent has been filtration (or ultra-filtration) through such a membrane as cellophane, the familiar transparent sheets of cellulose used in wrapping chocolates and certain high grades of soap. Dense membranes may be obtained through which a soap solution passes unchanged when it is in such dilution that conductivity and osmotic effect show it to be crystalloidal—that is, consisting of simple molecules and ions. The same membranes hold back all the soap, allowing only water to pass through, when the soap solution is sufficiently concentrated that, according to the argument already given, the soap is entirely in colloidal form, neutral and ionic micelles. Intermediate solutions can be tested for the amounts of crystalloidal and colloidal constituents. Further, membranes with pores of any size may be obtained whose diameter can be measured by the pressure required to blow air through them when wet; with these it is possible to hold back the neutral micelle, allowing the ionic micelle to pass through. It is evident that the membranes too have a micellar structure. Again, by using a reference substance such as salt, it is possible to measure the hydration of the colloid which is held back, by obtaining a filtrate which on occasion is twice as concentrated in reference substance as the original solution. In this way it is shown that the micelle contains about ten molecules of water for each equivalent of soap.

Throughout the foregoing discussion only solutions—that is, transparent fluids—have been discussed. The place that these colloidal electrolytes play in the general classification of all the

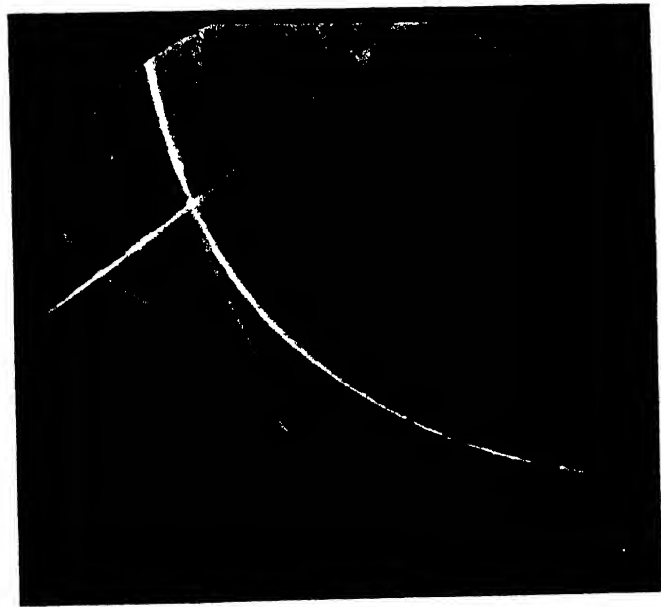


FIG 5.—1.0 N<sub>w</sub> SODIUM LAURATE, SHOWING CURD FIBRES  
AT ROOM TEMPERATURE

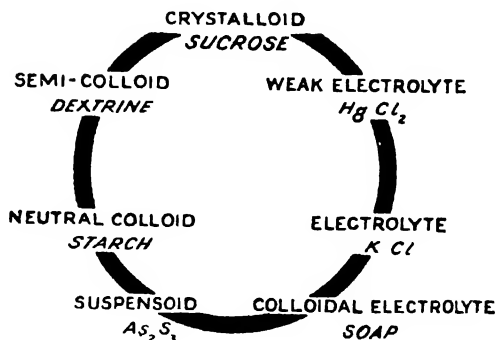


FIG. 6.—0.05 N<sub>w</sub> SODIUM BEHENATE SOLUTION,  
SHOWING FRESHLY FORMED CURD FIBRES.



FIG 7.—ULTRA-MICROSCOPIC APPEARANCE OF SUDDENLY  
PRECIPITATED BARIUM SULPHATE. (After von Weimann)

known varieties of solutions is shown in the accompanying diagram, where each type merges by gradual transition into the next.



#### STATES OF MATTER EXEMPLIFIED BY SOAPS AND THEIR SOLUTIONS.

All soaps under suitable conditions can occur in each of several crystalline forms, in two forms of liquid crystals or anisotropic liquids, and finally in certain cases the solutions previously described may set to form true transparent jellies. These true jellies are like gelatine jellies in that they are clear and elastic, and when not under strain they are isotropic--that is, dark between crossed nicols.

On the other hand, the anisotropic forms which occur in higher concentrations are not miscible with the isotropic solutions or jellies, but constitute separate phases. These doubly refracting liquids are not elastic but plastic--that is, they do not quiver when shaken, small portions do not flow under the influence of gravity, but passively remain in any position or shape which is given to them. These anisotropic liquids likewise have been found to be colloidal electrolytes. Their appearance, when examined between crossed nicols, is shown in figs. 1 and 2.

It is remarkable that when an ordinary soap solution sets to a true transparent jelly such properties as conductivity and osmotic activity are unchanged. It is evident that the same equilibria and the same particles exist in each. The jelly structure must be built up by the neutral micelles linking together by bonds of residual affinity (Trans. Faraday Soc., 1924, xx. 22) to form larger structures without losing their individuality. This well explains the reversible transformation of true jellies to soaps.

There are at least two crystalline forms of soap, lamellar crystals and curd fibres. This is well illustrated by the two photographs of

the same solution of sodium laurate crystallised in the two forms at room temperature, Figs. 3 and 4. Both give X-ray diagrams, whilst none of the other forms of soap solutions already described give radiograms. Figs. 5 and 6 illustrate again the appearance of curd fibres under the ultra-microscope. Fig. 7, which is strikingly similar, is taken from von Weimarn, and is likewise an ultra-microscopic picture of barium sulphate suddenly precipitated from concentrated solution. In all cases the curd consists of these innumerable crystalline fibres enmeshing mother-liquor.

Most of the substances of the type of soaps such as dyes, etc., exhibit many of the forms here described. Probably every soap can be brought into each of these states under suitable conditions. They exhibit a great family likeness, and the conditions differ merely in degree. All these phases are found in the two-component system water-soap, and it has been demonstrated that the phase rule applies to their equilibrium with each other. No new phases appear when salts are added.

The equilibria are surprisingly subject to law and order. Simple numerical rules relate the action of various electrolytes with each other independent of the nature of the soap. Again, simple rules hold for all soaps and their mixtures. It follows that the behaviour of the highly complicated mixtures of saponified oils and fats with various electrolytes met with in soap-boiling can be treated largely on the simple basis of a three-component system. Thus by phase-rule models it is possible to follow and predict quantitatively all the soap-boiling processes.

In conclusion, the writer would express the hope and expectation that when various investigators have carried out sufficient careful and many-sided work with a number of definite typical materials, like the soap which has been taken here as an illustration, the theory of colloids will ultimately become an exact science in which every statement will rest upon direct demonstration or quantitative proof.

[J. W. McB.]



Friday, March 27, 1925.

SIR JAMES CRICHTON-BROWNE, J.P. M.D. LL.D. D.Sc. F.R.S.,  
Treasurer and Vice-President, in the Chair.

SIR ERNEST RUTHERFORD, LL.D. D.Sc. F.R.S. M.R.I.,  
Prof. of Natural Philosophy, R.I., Cavendish Prof.  
of Exptl. Physics, University of Cambridge.

### Studies of Atomic Nuclei.

[ABSTRACT RECEIVED APRIL 6, 1925.]

It is well known that a study of the single scattering of  $\alpha$  particles by the elements led to the nuclear theory of the atom, and has provided us with a direct method of measuring the nuclear charge of the elements. The pioneer experiments in this field were made by Geiger and Marsden in 1913, who showed that the number of particles scattered at different angles was in close accord with the nuclear theory, assuming an inverse square law for the forces between the  $\alpha$  particle and the nucleus. The variation of scattering with velocity of the  $\alpha$  particle was in close accord with this law. Their results were subsequently extended by the experiments of Chadwick, who made direct measurements of the nuclear charge. Most of the experiments of Geiger and Marsden were made with silver and gold. Using  $\alpha$  particles of average range about 4 cms. of air, they found that the law of inverse square held, at any rate approximately, for the closest distance of approach of the  $\alpha$  particle—viz. about  $4 \times 10^{-12}$  cms. for gold. These results suggested that the nuclei of even the heavy elements must be of radius less than this small distance.

In a collision of an  $\alpha$  particle with a light atom the distance of approach in a close collision is much smaller than the above, and direct evidence has been obtained that the law of the inverse square breaks down completely in the case of a close collision between an  $\alpha$  particle and a hydrogen nucleus. More recently Bieler compared the scattering of  $\alpha$  particles by aluminium and gold, and found the relative number of particles scattered by aluminium and gold to decrease as the angle of scattering was increased. Assuming that the scattering by gold was normal—i.e. in agreement with an inverse

square law—he suggested that the discrepancy in aluminium might be due to the combined action of an attractive force superimposed on a normal repulsive force. From calculation he concluded that an attractive force varying as  $r^{-4}$  fitted in best with his experimental results. In the light of these conclusions it became of importance to re-examine the question whether the law of inverse square holds accurately for the heavy elements for the closest possible distances of approach, and to determine as accurately as possible the variation of the scattering with velocity for the lighter elements.

For this purpose, Dr. Chadwick and I have used a modified method, and examined for a number of elements the scattering at an angle of about  $135^\circ$ , for  $\alpha$  particles of different velocities. The source of  $\alpha$  rays (radium B and C deposited on a metal disc) was hermetically sealed in a brass tube covered at one end by a thin film of collodion of stopping power about 2 to 3 mm. of air for  $\alpha$  rays. This was necessary to avoid radio-active contamination. The  $\alpha$  rays fell on the radiator of small area of stopping power 2 to 5 mms. of air carried on a frame of Acheson graphite. Extra care was taken to avoid extraneous scattering. By introducing thin sheets of mica of known stopping power in the path of the  $\alpha$  rays, the variation of the number of  $\alpha$  particles with velocity was directly determined. In this way measurements were made for  $\alpha$  particles between the ranges of 6.7 cms. and 2 cms. The straggling of the  $\alpha$  particles in their passage through the mica made this method unreliable for shorter ranges of the  $\alpha$  particles.

In this way it was found that the number of particles scattered by silver and gold through an average angle of about  $135^\circ$  varied inversely as the square of the energy of the incident  $\alpha$  particles over the whole range. In the case of gold measurements were also made for smaller angles by the direct method of measuring the nuclear charge, previously used by Chadwick, and no variation in the law of the inverse square could be observed. Similar results were observed with a thin film of uranium obtained on graphite by sputtering. In this case it was difficult to determine the actual thickness of the film, but the variation in number of scattered  $\alpha$  particles with velocity followed the regular law.

In the case of aluminium an unexpected result was observed. The scattering for 6.7 cms.  $\alpha$  particle was less than the theoretical, and rapidly *decreased* as the velocity of the  $\alpha$  particles was diminished, falling to a minimum for particles of range about 5 cms. It then increased again and tended towards the theoretical value for slow-speed  $\alpha$  particles. It is of interest to note that the velocity of the  $\alpha$  particles for this minimum of scattering is about the same as the minimum velocity required to liberate protons from aluminium. It should be mentioned that even for the swiftest  $\alpha$  particle the number of protons of range greater than 3 cms. which appeared at an angle of  $135^\circ$  was only a small fraction of the total number of scattered

$\alpha$  particles, indicating that the expulsion of a proton does not occur in all close collisions of the  $\alpha$  particle with the nucleus.

From the observations on the scattering by a film of uranium, it is clear that the law of inverse squares holds, at any rate approximately, up to the closest distances of approach—viz. about  $3 \times 10^{-12}$  cms. This raises a difficulty, since from radio-active evidence it is believed that the nuclear structure of uranium extends to a distance of about  $7 \times 10^{-12}$  cms. If the  $\alpha$  particle liberated in the disintegration of uranium gains most of its energy in escaping in the repulsive field of the nucleus, its position before disintegration cannot be less than  $7 \times 10^{-12}$  cms. from the centre of the nucleus, and may be greater if it is liberated with initial energy. It is for this reason that it has been considered probable for some time that the radio-active elements consist of a central charged nucleus surrounded at a distance by a satellite distribution of positively and negatively charged particles. If these form a symmetrical doublet-like structure extending over a short linear distance, it may be difficult to detect the presence of such a satellite distribution by direct scattering experiments. A similar idea may be used to explain the peculiar behaviour of the aluminium nucleus. In such a case the distance apart of the satellites or doublets may be comparable with their distance from the main nucleus. It is easy to see on such an assumption that  $\alpha$  particles of appropriate speed may just enter the satellite region where the electric field may be relatively weak, and thus show a marked defect in scattering. Swifter particles pass through the satellite distribution and come under the strong electric field of the central nucleus, where they are more effectively scattered.

It is obvious that an accurate determination of the scattering of  $\alpha$  particles by the elements may supply important evidence, not only on the size of the nucleus, but on some of the details of its structure. A large amount of accurate data will be required to test the adequacy of any theory of nuclear structure.

Since the proof that protons can be expelled from the nuclei of many light elements, the fate of the bombarding  $\alpha$  particle after the disintegration has been a matter of conjecture. To throw light on this question Blackett has recently photographed by the well-known expansion method the tracks of more than 400,000  $\alpha$  particles in nitrogen. In addition to a number of branching tracks which obey the laws of a perfectly elastic collision, eight branching tracks were observed in which the laws of an elastic collision were not obeyed. In these photographs the fine track of the proton was clearly visible, and also that of the recoiling nucleus, but in no case was there any sign of a third branch due to the escaping  $\alpha$  particle. He concluded that the  $\alpha$  particle was captured in a collision which led to the ejection of a proton. The branches were co-planar, indicating that momentum was conserved in such collisions. The length of the tracks of the proton and recoiling nucleus was in good accord with

such an assumption. These experiments suggest, at any rate in the case of nitrogen, that the  $\alpha$  particle is captured by the nucleus. If no electron is expelled, the resulting nucleus should have a mass  $14 + 4 - 1 = 17$ , and a nuclear charge  $7 + 2 - 1 = 8$ —i.e. it should be an isotope of oxygen. It thus appears that the nucleus may increase rather than diminish in mass as the result of collisions in which a proton is expelled.

[E. R.]

Friday, May 1, 1925.

SIR EDWARD POLLOCK, F.R.C.S., Manager and Vice-President,  
in the Chair.

W. L. BRAGG, M.A., O.B.E., F.R.S., Langworthy Professor of  
Physics, Victoria University of Manchester.

### The Crystalline Structure of Inorganic Salts.

THE examination of crystalline bodies by means of X-rays has enabled us to discover the positions of the atoms in the crystal. In the earlier period of X-ray analysis it was only possible to do this when the atoms were arranged according to a simple pattern of high symmetry. Experience has increased the range of substances to which the new methods can be applied, and we can now assign structures to relatively complex crystals, basing the proposed structure on the manner in which the crystal diffracts the radiation.

The study of the crystalline structure of organic and inorganic compounds has revealed certain broad distinctions between these two classes of crystals. The crystalline arrangement throws new light on those differences in the structure of the molecule which have made it convenient to distinguish organic from inorganic chemistry. No exact line can be drawn between the two classes of crystals, and yet the main features are sufficiently different to make the classification useful. The organic crystal appears to be composed of definite molecules. Inside each molecule the atoms are bound together by forces so local, and so rigid, that an addition to one part of the molecule hardly affects the rest; these molecules are then massed together by comparatively weak forces into a crystalline structure. The form of the inorganic crystal suggests that the bonds between atom and atom are not limited to certain directions; the molecule is more fluid, and an addition to one part profoundly disturbs the relationship of all the rest. It must be this molecular fluidity which makes it so hard to apply the ideas of stereochemistry to inorganic compounds, although they have been so successful in explaining the organic compounds.

Our powers of X-ray analysis are as yet very incomplete, and it is difficult to find the positions of the atoms in complex structures. The complexity of a structure depends on the number of parameters, or degrees of freedom permitted by the symmetry, which fix the positions of the atoms in its pattern. At the present time any structure with more than half a dozen of these independent parameters presents a difficult problem; whereas crystals with two or three parameters are comparatively simple. For several reasons the inorganic salts can be analysed more completely than organic compounds. In the first place, the number of atoms in the inorganic molecule is generally smaller than that in the organic molecule, and owing to the power of re-adjustment in the former class of compound which has already been mentioned, the atoms often take up a symmetrical arrangement, and this symmetry makes the X-ray investigation more easy. Every requirement of symmetry which must be satisfied by the atom reduces the number of variable parameters in the structure, and confines the atom to certain planes, lines, or points from which it cannot move. Further, in a series of inorganic crystals it is often possible to replace one atom by another of similar chemical properties without altering the crystalline structure. Now the heavier atoms scatter X-rays more than the lighter atoms. If, therefore, we wish to find the position of the metal atoms in an inorganic salt, and a crystal of the series is available in which the metal has a high atomic weight compared with the other constituents, it is an easy matter to fix its position. The same process can often be carried out with a heavy atom in the acid radical and a light one in place of the metal. In order to aid the X-ray examination we are using a method which is precisely like the staining, by means of suitable dyes, of certain parts of a microscopic preparation. In the organic crystal the atoms of carbon, oxygen, and nitrogen are almost indistinguishable by means of X-rays since they are so close in the periodic table, and with the exception of one or two compounds it has so far been impossible to fix their positions.

The inorganic salts are interesting, not only because we know more about their structure, but also because they lend themselves more readily to mathematical treatment. We may compare this case of crystal equilibrium to the engineering problem of calculating the stresses to which the members of a girder system are subjected. If the number of constraints is the minimum requisite for rigidity, these stresses can be directly calculated by simple laws of mechanics. If the whole structure is too rigid, much more detail must be known about the structure in order to calculate the stresses. The inorganic crystal represents the structure with the minimum number of constraints. We can try and explain the properties of the crystal as a whole by making certain simple assumptions about the forces between the atoms. It is certain that the real atomic properties

are more complex than those represented by these simple assumptions, but it is interesting to see how far one can get towards an explanation with their aid. One can, for instance, explain a number of crystalline properties by assuming an atomic model of the following kind :—

(a) The atom consists of a symmetrical electronic structure surrounding the nucleus in which the charges on the electrons and on the nucleus do not balance, so that the sum of the charges is sometimes positive, sometimes negative.

(b) When the atoms approach within a certain distance of each other a force of repulsion between their outer electronic structures sets in very rapidly and prevents closer approach.

(c) When the atom is placed in an electric field it becomes polarised. Its positive and negative parts are drawn in opposite directions, and it is surrounded by a field like that of an electrical doublet.

With the aid of these assumptions qualitative explanations have been given of the formation of inorganic compounds (Kossel) and quantitative explanations of the heats of formation, heats of solution, latent heats of evaporation, and elastic properties of the inorganic crystals (Born and Lande, Madelung, Fajans, and others). Their highly interesting investigations have been applied to crystals of a symmetrical and simple type, such as the rock-salt structure. The quantitative agreement between calculated and observed data is most striking, and shows that the assumptions which have been made are not far from the truth. I do not wish to discuss their results here; I quote them to show how far this atomic model explains the facts, as I wish to use it in examining the more complex salts which we have analysed by X-rays.

The force which causes two atoms to repel each other when they approach closely is very interesting. We do not know its origin, but it is clear that it sets in very sharply and increases rapidly as the centres of the atoms get closer together. This is so much the case that each atom in the crystalline structure appears to be surrounded by a domain which it occupies to the exclusion of other atoms. We cannot define the size of this domain exactly, because the distance of closest approach of two atoms will always depend on the strength of the force driving them together, but the domain varies within narrow limits for the range of forces ordinarily present in a crystal. A knowledge of the domain associated with the atoms and molecular groups is most important in crystal analysis, since it limits the possible configurations and confines the atoms to certain regions where they do not overlap too greatly. In a Friday evening discourse four years ago I gave some empirical figures for the radii of these atomic domains, and tried to show how these figures could be used to aid crystal analysis. I wish to take this opportunity of saying that I have considerably

altered my views on this question. Other workers who have dealt with the subject have given alternative estimates of the domains which I believe to represent the physical facts far better than did my original figures; and, in addition, a more complete knowledge of crystal structures has shown how elastic the atomic domain is and what care is necessary in using the conception to help analysis. Nevertheless, its very great importance must not be lost sight of, for it is one of the principal aids we have in tackling a difficult crystal structure.

We do not know the exact dimensions of the electronic orbits, but such estimates as can be formed suggest that in a crystal such as rock-salt there are large spaces between the outermost orbits of neighbouring atoms. Each atom has its system of orbits quite distinct and widely separated from those of its neighbours. This is generally true where the charged atoms are of a symmetrical type and held together by electrostatic attraction. On the other hand, where the chemical evidence points to a linkage of the homopolar type, crystal analysis shows the atoms close together as if the electronic orbits were actually linked up.

A series of atomic structures such as  $O^{--}$ ,  $F^-$ ,  $Ne$ ,  $Na^+$ ,  $Mg^{++}$ ,  $Al^{+++}$ , are supposed by Kossel to have a common configuration resembling that of neon itself. The charges on the atoms are due to the addition or removal of electrons required to give them the correct number for a neon structure. The scale on which the atoms are built must diminish from oxygen to aluminium, owing to the increasing nuclear charge,  $Al^{+++}$  being on about one-half the scale of  $O^{--}$ . The idea of an atomic domain can only be a very rough approximation to the truth, for in actual fact there must be a different law of force for every given pair of atoms: in this approximate sense, interatomic distances in simple crystalline structures are in agreement with the supposition that they obey an additive law, and that the dimensions of the domain are proportional to those of the atomic structures in a series such as has been given above. I drew attention to this additive law as an empirical fact in the discourse referred to above, but made the domains of the positive ions too large and those of the negative ions too small. A better interpretation of the significance of the law was given by Wasastjerna in a paper on the "Radii of Ions," in which due weight was given to the relative dimensions of the electronic structures. Recently Jones in a series of highly interesting papers has linked up the fields which give the repulsion between atoms of an inert gas, and the fields of the corresponding ionic structures in crystals.

In the case of the very simple crystals good quantitative agreement between calculation and observation of crystal dimensions can be obtained by certain simple assumptions about the nature of the repulsive field due to their electronic structures. In the more complex crystals the concept of an atomic domain is by itself sufficient



to explain the general configuration of the crystal. Cases which are especially interesting are those where the domain of one ion is much larger than that of the other. The structure of aluminium oxide,  $\text{Al}_2\text{O}_3$ , is an example. Since the oxygen ion is so much larger than the aluminium ion, the structure is that of a series of oxygens in a close-packed arrangement (hexagonal), with aluminium atoms in the interstices acting as a cement to bind the whole together. In spinel,  $\text{MgAl}_2\text{O}_4$ , the oxygen atoms are in a cubic close-packed arrangement. In cadmium iodide,  $\text{CdI}_2$ , the large iodine atoms are in hexagonal close-packing with cadmium atoms lying between alternate layers perpendicular to the hexagonal axis. Tin tetraiodide is another case where a quite complex structure approximates closely to a cubic close-packed arrangement of iodine atoms. Such crystals give a great deal of information about the forces between atom and atom.

In a few cases it has been possible to determine the shape of the acid radical. In  $\text{CO}_3^{--}$  and  $\text{NO}_3^-$  the oxygen atoms are arranged at the corners of an equilateral triangle around the central atom, and the arrangement must be very nearly the same in  $\text{ClO}_3^-$ . Though we do not know the arrangement of the oxygen atoms round the sulphur atom in  $\text{SO}_4^{--}$  with such certainty, they must be nearly at the corners of a regular tetrahedron, and the arrangement also holds in such groups as  $\text{ClO}_4^-$ ,  $\text{MnO}_4^-$ ,  $\text{SeO}_4^{--}$ . In an ion such as  $\text{PtCl}_6^{--}$  Wyckoff has shown that the six chlorine atoms are arranged at the corners of a regular octahedron around the platinum atom. The simple geometrical shape in each case is interesting, and it is difficult to avoid the conclusion that the outer atoms are all related in the same way to the inner one. Kossel regards the inner atom as having a large positive charge, and holding the negatively charged outer atoms by electrostatic attraction. Although the actual bonds may be of a more complex type, it is interesting to see how much this idea explains. The dimensions of the group are in accord with the idea that the large oxygen ions are grouped around a relatively small atomic structure with a high positive charge in the centre, and that the size of the group is mainly determined by the repulsive forces between the oxygens. Certain optical properties can be explained by the same conception. The refractivity of the acid group is got by assigning a value of about 3.3 to the ionic refractivity of each oxygen, and a very small value to the central atom. The strong negative double refraction of carbonates and nitrates, where the groups of oxygen atoms lie in parallel planes, is explained quantitatively by the influence on each other of the oxygen atoms arranged in a triangle. On the other hand, most sulphates have a very small birefringence. This may be explained by the regular tetrahedral arrangement of oxygens around the sulphur, for such a group on account of its symmetry is practically isotropic.

The problem of the other type of binding between atoms, in which the electronic structures seem to fuse together so that the

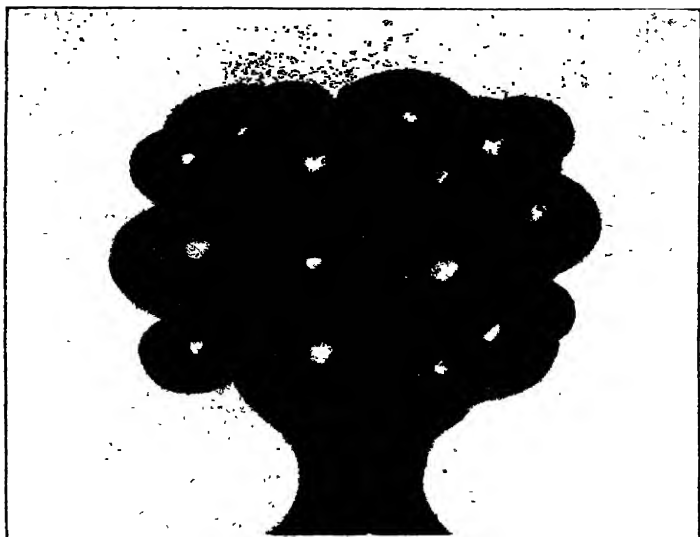


FIG. 1.

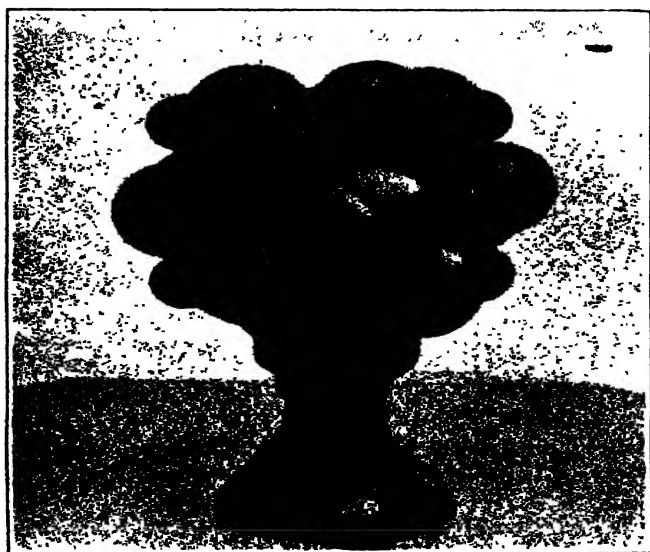


FIG. 2.

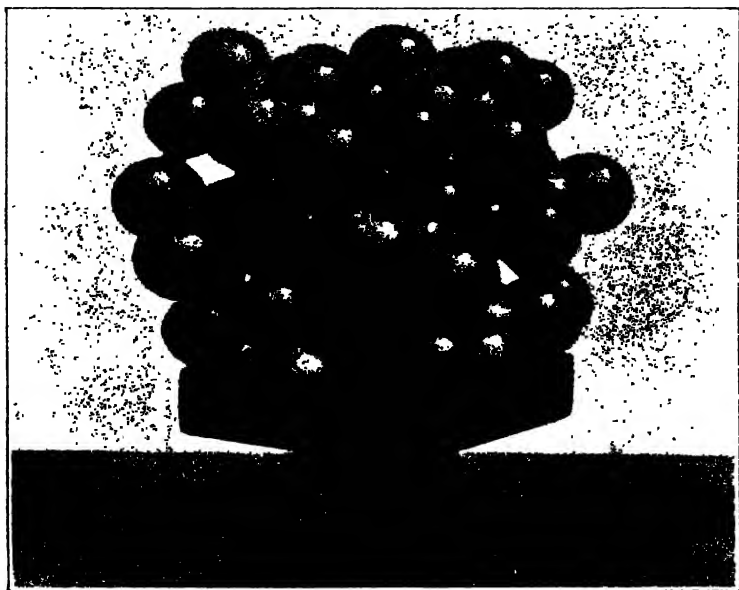


FIG. 3.

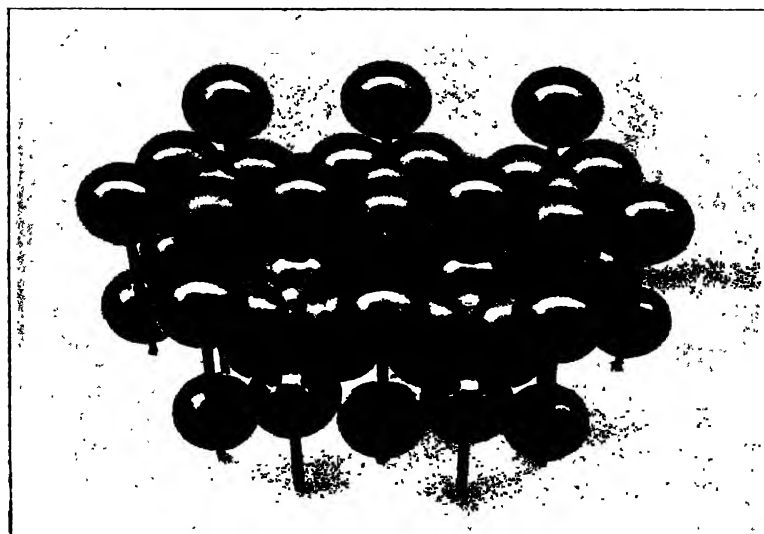


FIG. 4.



FIG 5



FIG 6.

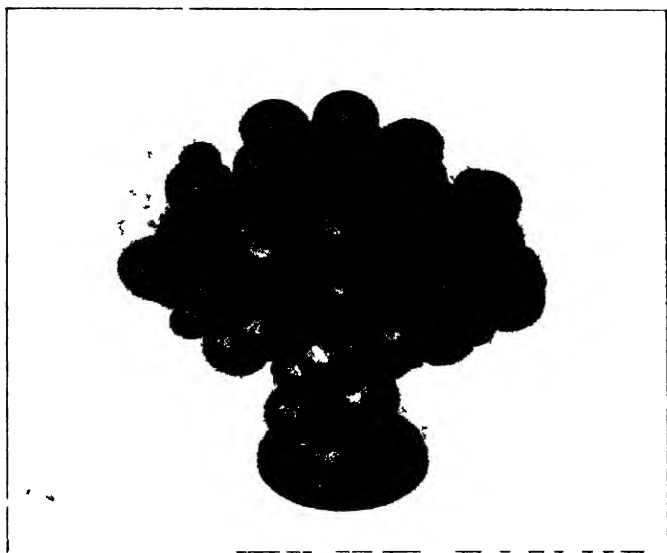


FIG 7.

atoms approach each other closely and are rigidly connected, has yet to be solved. In acid groups such as  $\text{CO}_3^{--}$  and  $\text{SO}_4^{--}$  the atoms may retain separate electronic systems, or the other type of binding may have come into play. In any case the atoms must be greatly distorted by their unsymmetrical location. X-rays can only tell the positions of the atomic centres, the skeleton of the structure, since the interference between waves scattered by the electrons is so complex. The centres can be fixed with considerable certainty, however, and cases of undoubted homopolar combination can be examined. The interest of the inorganic structures lies principally in the fact that they can be analysed with some degree of completeness, and it is to be hoped that they will tell more about the binding forces. They present a fascinating series of problems for solution.

#### NOTE ON CRYSTAL MODELS.

Figures 1-7 are reproductions of models made to a scale of one centimetre to the Ångström unit ( $10^{-8}$  cm.). The atoms are represented by spheres, whose centres are at the positions found by X ray analysis. An attempt has been made to represent the size of the atomic domain in order to show the usefulness of this conception as an aid to crystal analysis. The following figures for the radii of the spheres in centimetres have been used :—

O- - 1.35	F- 1.30	Na+ 1.05	Mg+ + 0.75
S- - 1.75	Cl- 1.75	K+ 1.35	Ca+ + 1.05
Se- - 1.95	Br- 1.95	Rb+ 1.50	St+ + 1.20
Te- - —	I- 2.15	Cs+ 1.70	Ba+ + 1.40

In simple salts of the rock-salt or fluor-spar type the interatomic distances are given quite accurately by the sum of these figures. The figures correspond closely with those given by Wasastjerna.\*

The sizes taken for the more compact metallic ions are as follows :—

Li+ 0.80	Cu+ 0.55	Ag+ 1.00		
Be+ + 0.45	Fe+ + 0.70	Mn+ + 0.75	Zn+ + 0.60	Cd+ + 1.00

In the case of these ions the simple additive law is more widely departed from, and the figures are only given to show that the ion must be supposed to have small dimensions.

A comparison of the molecular volumes of isomorphous crystals shows that  $\text{NH}_4^+$  and  $\text{Tl}^+$  have the same dimensions as  $\text{Rb}^+$ , and that the same is true for the pairs  $\text{Pb}^+ +$  and  $\text{Sr}^+ +$ ,  $\text{CN}^-$  and  $\text{Br}^-$ ,  $\text{OH}^-$  and  $\text{F}^-$ .

\* Wasastjerna. On the Radii of Ions (Soc. Scient. Fenn., Comm. Phys.-Math., vol. 1, p. 38, 1923).

The following models are reproduced in the illustrations :—

1. ROCK-SALT,  $\text{NaCl}$ .—The smaller spheres represent the sodium ions and the larger spheres the chlorine ions.
2. IRON PYRITES,  $\text{FeS}_2$ .—The sulphur atoms appear to be bound together by a homopolar link, since the distance between them is so small ( $2.05\text{\AA}$ ), whereas the repulsive field between two separate  $\text{S}^-$  ions would assume a large value at a distance of about  $3.5\text{\AA}$ . The  $\text{S}_2$  group is represented as having two overlapping domains, as shown in the figure. This is equivalent to assuming that each sulphur atom repels other atoms, as if it were a separate  $\text{S}^-$  ion, in all directions except that in which it is closely linked up to its companion S atom. The  $\text{FeS}_2$  crystal is a very compact arrangement of Fe atoms and  $\text{S}_2$  groups. The domains of the latter touch in all directions as if the volume of the crystal were mainly determined by the repulsion between these large groups.
- 3 & 4. CALCITE AND ARAGONITE,  $\text{CaCO}_3$ .—In both of these forms of calcium carbonate the  $\text{CO}_3$  group consists of three oxygen atoms surrounding a central carbon atom at a distance of about  $1.25\text{\AA}$ . The oxygen atoms are represented by spheres of  $1.35\text{ cm. radius}$ , overlapping where they touch each other, and are attached to the carbon at the centre.
- 5 & 6. ALUMINIUM OXIDE AND SPINEL,  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$ .—In these crystals the large oxygen ions are arranged compactly, in an approximation to hexagonal close-packing in the first case and to cubic close-packing in the second case. The smaller ions of magnesium and aluminium fit into the spaces between the oxygen ions.
7. LITHIUM POTASSIUM SULPHATE,  $\text{LiKSO}_4$ .—This structure, as analysed by A. J. Bradley, is given to show the form of the  $\text{SO}_4$  group. Four oxygen atoms surround a central sulphur atom at a distance of between  $1.3$  and  $1.5\text{\AA}$ . The ion  $\text{SO}_4^{--}$  is much the largest component in the crystal structure, and it is interesting to note that the ions regarded as units are approximately in close-packed hexagonal array.

[W. L. B.]

Friday, May 15, 1925.

SIR DUGALD CLERK, K.B.E. LL.D. D.Sc. F.R.S.,  
in the Chair.

CHARLES G. DARWIN, M.A. F.R.S.,  
Tait Professor of Natural Philosophy, University of Edinburgh.

### Recent Developments in the Theory of Magnetism.

THERE have been several important discoveries made in the theory of magnetism in the course of the last two or three years, and we shall discuss some of these: but in order to appreciate them it will be well to begin with a description of the general magnetic properties of matter. All magnets can be typified by the ordinary bar magnet, which has a north pole at one end and an equally strong south pole at the other. If such a magnet is cut in two the north half grows a south pole at the section and vice versa. In consequence of this we do not take the magnetic pole as working unit, but the magnetic dipole. We imagine that each molecule of the bar has north and south poles, and that they are ranged end to end, so that all the middle ones cancel out and leave a free north pole at one end and a free south at the other. The measure of a magnet is then taken, not as the pole strength, but as the *magnetic moment*, which is the product of the pole strength into the length. The moment of the whole bar is the sum of the moments of its molecules.

There are two chief ways in which magnetic effects exhibit themselves. The first is that shown by a compass when it twists round so as to point along the direction of the earth's field. There is another effect which is very important, and to be distinguished from it, which arises when the field is not uniform. Then one end of the magnet will be pulled more than the other is pushed, and so the magnet will experience a force moving it bodily—this may be either an attraction or a repulsion. The first effect is usually easier to exhibit, but we shall be more concerned with the second.

Under the influence of a magnet all bodies become themselves magnetic, but there are three quite distinct types of behaviour. A piece of iron becomes strongly magnetic with an S pole next the N pole of the inducing magnet. Iron, nickel, and one or two other substances have this property to a high degree, but there are many others, for example aluminium, which show it feebly. For all these it is about a hundred million times less, and so a different name is



used. Iron, etc., are said to be ferro-magnetic, the rest are called paramagnetic. If a paramagnetic rod is put between the poles of an electro-magnet it becomes itself a feeble magnet with north pole next to the south pole of the inducing magnet. There exist many other substances, for example copper, having the opposite property. Facing the north pole of the electro-magnet there appears a feeble north pole. This property is called diamagnetism. The measure of the two properties is called *susceptibility*, and is positive for paramagnetic and negative for diamagnetic substances. It is found by making experiments in non-uniform fields. A paramagnetic substance tends to move into the strong field, a diamagnetic out of it. So a bar hung between pointed pole pieces will twist round towards the points in the first case and away from them in the second.

Magnetic action is exhibited by electric currents, as is typified by the galvanometer and every ordinary electrical measuring instrument. Now, in science one cannot admit that two radically different things can produce identical effects, so we are forced to conclude that either the current is really a magnet, or the magnet is really a current, and the second is certainly the correct alternative. In each iron atom there is a current circulating, and this current gives rise to its magnetic moment. We shall see now how this explains dia- and paramagnetism, taking for simplicity the supposition that we are dealing with a gas.

Suppose that we surround a cylinder of metal by a wire and then put current through the wire. The current causes a magnetic field along the axis. At the moment of making, an eddy current will be induced in the cylinder in the opposite direction, but the frictional resistance to the flow of electricity will destroy this quickly. Now if there were no friction (as is actually the case at very low temperatures) this current would persist indefinitely, and would exert a magnetic field weakening the other. This is exactly what diamagnetism does. So we say that the atom is somehow like a frictionless conductor. When a field is put on, it induces opposing currents in the atoms, and these persist and exert a field opposing the external field.

We must next explain paramagnetism. We believe that every atom has the induced current of diamagnetism, but that this is over-ridden by a second property. Each atom of a paramagnetic gas has a magnetic moment, even when there is no field. If we could suppose them to be little bar magnets they would swing to and fro in the presence of an external field, and would be oftener pointing down the field than up it. This would give an extra magnetic moment down the field, and would be paramagnetism. Unfortunately the matter is not so simple as this, because the moment must be caused by a revolving electron, and this behaves quite differently. It may be likened to a top, which has the property of always moving at right angles to the direction in which it is pulled. So our atom will not

go towards the field at all but will precess round it, and there will be no gain of magnetic moment in the direction of the field. In order to get this gain we have to allow for collisions between the atoms, for then the axes of the tops will be able to change, and will, in fact, have the tendency to point oftener towards than away from the field. The amount of the effect may outweigh the diamagnetism which is always present. The phenomenon shows a clear sign that it depends on collisions, for whereas diamagnetism is constant, paramagnetism depends on the temperature. When the gas is hot, the violence of the collisions makes nearly as many molecules point away as towards the field, but when it is cold the gentle collisions allow them nearly all to settle down along the field.

There is a most difficult point in the argument which is rather too abstruse to explain in detail. It turns on the proper way of taking the averages of the moments of the atoms. This must be carried out with the greatest rigour from dynamical principles. In the past many writers tried to make short cuts and obtained a variety of results. Some proved there could be no paramagnetism, some no diamagnetism, and some even that there could be neither. The essential point of the argument is that the atom must have somewhere the property of a top, which goes on spinning at the same rate however its axis may be altered.

The question arises as to whether there would be any way of observing the magnetic moment directly. Such a way was suggested by Stern about three years ago, and the experiment which he carried out in conjunction with Gerlach is certainly one of the most remarkable of the present century. In a vacuum an atom of gas will go in a perfectly straight line till it hits the wall. If a source of atoms is in line with two fine slits they will all hit the opposite wall in a narrow line. The atoms were obtained by boiling silver in a small furnace. Those which get through the slits strike the wall and stick there. Even after four hours nothing is visible on the glass, but there exist chemical methods of development whereby the invisible trace of silver attracts more silver from the developer and becomes visible. Now suppose that in their path the atoms encounter a non-uniform magnetic field. In the gaseous form the atoms of silver have a magnetic moment, and so they will experience a deflecting force. If the atoms were pointing arbitrarily in all directions, the character of the field shows that the fine line of the image should be spread out into a lens-shaped figure. What is in fact observed is quite different; the lens is there, but it is hollow. The atoms are all pointing straight towards or straight away from the magnetic field.

This result would have been astonishing twenty years ago, but as a matter of fact the experiment was tried with a fairly strong expectation that it would turn out as it did. The quantum theory has illuminated many branches of physics, but none more than spectroscopy, and in particular it describes with complete success

the influence of magnetic fields on spectra. According to this theory the atom is a very definite structure, and the definiteness extends not merely to size and shape, but also to its direction in space. The theory goes further and indicates that an atom ought to have a definite magnetic moment (which is called the "Bohr magneton"), or in some cases a simple multiple or fraction of this. In silver the deflection corresponds exactly to one magneton. Several other substances have since been measured, and most of the effects explain themselves on the same principles. Modern physical theory has to face a great many difficulties, and one of the severest is to explain how it is that half the atoms can point away from the field. Each atom evaporates in the furnace right outside the magnetic field and pointing in an arbitrary direction. As it enters the field, if it is to point away, it must gain energy, and there is nowhere from which the energy can come. This would have been a severe difficulty a few years ago, but dynamical toleration has grown recently, and it is becoming recognised as a probability that energy is only conserved on the average and not exactly.

The older calculations of para- and dia-magnetism depend essentially on assuming that the atoms can point in any direction, and they go wrong if this ceases to be true. We know it to be untrue in Gerlach's experiments, and the question arises as to whether it is true in other cases. This is the subject of some very remarkable recent experiments by Glaser. The susceptibility of gases is very small and hard to measure unless the gases are compressed. Glaser has perfected the arrangements of one method of experiment to such a high degree that he could measure the effect for very low pressures. The principle of his experiment can be described by analogy with the question of buoyancy. If a body is weighed in air and in water the difference of the weights measures the weight of the displaced water. If a different liquid is used a similar weighing will give its density in terms of water. Glaser takes a light rod of some substance, actually a slightly paramagnetic glass, and suspends it in a non-uniform field. In a vacuum the field twists the rod round by a definite amount. If it is surrounded by a gas which is also paramagnetic it will not experience as great a twist, because it will, so to speak, be partly floated by the gas. Similarly if the gas is diamagnetic it will be more twisted than in a vacuum. The effect is very small and by no means easy to obtain, but by measuring the amount of twist a value can be found for the susceptibility. The diamagnetism stays constant down to a fairly low pressure, and then changes over to a larger value, actually three times as great. The work is very recent, and the theory is still more or less unknown. Superficially the phenomenon is rather like that of Gerlach, but a little deeper consideration shows that no very close analogy can be drawn between the two cases. It is natural to suppose that the collisions between the molecules are somehow responsible for reducing

the susceptibility at high pressures. The only suggestion, that can at present be made to fit the facts, is to suppose each atom like a plate, which sets itself edgewise to the field after each collision, and then gradually turns through a right angle and settles down along the field. This is very unnatural; we do not think an atom is like a plate, and also we should expect that the collisions would not set the atoms edgewise, but would simply disorientate them, and this would only produce half the observed change of susceptibility. No doubt there will soon be more experiments to help us. For example, much could be deduced if we knew how the curves varied for different temperatures; and it would also be most interesting to know how other gases behave, in particular the strongly paramagnetic oxygen. Unlike the work of Stern and Gerlach, Glaser's experiments do not seem to fit in with the general scheme of things, and so we may perhaps hope that they will lead to some surprising new developments in physical theory.

[C. G. D.]

Friday, June 12, 1925.

SIR EDWARD POLLOCK, F.R.C.S., Manager and Vice-President, in the Chair.

SIR WILLIAM J. POPE, K.B.E. LL.D. D.Sc. F.R.S. M.R.I.,  
Professor of Chemistry, University of Cambridge.

### Faraday as a Chemist.

MICHAEL FARADAY was born in 1791, the son of a working blacksmith in London. During the distress of 1801, when corn rose to over £9 a quarter, his family received public relief, and one loaf of bread was allotted weekly to the nine-year old child. His systematic education was rudimentary in character, for in his thirteenth year he became errand-boy to a bookseller in the neighbourhood of Manchester Square, and was entrusted with the duty of distributing the Sunday newspapers.

So lowly an introduction to life might seem to furnish but a slight foundation for a great scientific career. Yet Faraday became Director of the Laboratory of the Royal Institution in his thirty-fourth year, and succeeded Sir Humphry Davy in the Chair of Chemistry in 1827; on his death in 1867 he was mourned by practically every learned academy in the civilised world as one of the foremost of the great chemists and physicists of the first half of the nineteenth century. Many of Faraday's discoveries and much of his mode of interpreting chemical observations still persist as sources of inspiration to the chemist of a century later. The task of tracing the career of this great scientific luminary, of trying to decipher the stages in his major discoveries and of learning how his dominating position in science was attained, is an interesting one; it is an illuminating one as showing how the exercise of industry and ability can reduce to negligible proportions the effect of faulty early education and of absence of family support.

Faraday was apprenticed as a bookbinder to his employer in 1805; his indentures note that "in consideration of his faithful service no premium is charged." He has told us that whilst an apprentice he read a great number of scientific books which came under his hands, and the correspondence which he left shows that he was in the habit of discussing with keen enthusiasm a large variety of scientific topics; he attended a few lectures on natural philosophy by certain private

individuals who were in the habit a century ago of advertising such discourses. Early in 1812 a customer of his master's shop enabled him to attend four of Sir Humphry Davy's lectures in this theatre ; we are told that he sat in the gallery just above the clock, and that he carefully elaborated his notes upon the experiments shown and the explanatory discourses. Faraday's contemporary correspondence makes it clear that he became captivated by the charm of manner and the skill in exposition and experiment of the master ; he got into contact with Davy, and on March 1st, 1813, was appointed by the Managers as assistant in the Laboratory of the Royal Institution.

Faraday's scientific career had commenced, but it had commenced in circumstances which would have discouraged any but the most intrepid. The first piece of work in which he was called upon to assist Davy consisted in experiments on the newly discovered nitrogen chloride ; six weeks after he came to the Royal Institution he was writing to a friend describing the injuries from which he and his master were suffering by the premature explosion of this capricious substance. Although this frequency of bodily hurt must have been very disconcerting to an entire novice in chemical experiment, Faraday seems to have accepted it without demur or complaint, and as a necessary incident to the occupation which he had now definitely determined to adopt. Indeed, a month later he writes his friend at some length, and with no little perspicacity, upon the conduct of lectures and the behaviour of lecturers. He observes that "polite company expect to be entertained not only by the subject of the lecture, but by the manner of the lecturer ; they look for respect, for language consonant to their dignity, and ideas on a level with their own." This youth of twenty-one years of age was by no means unprecocious ; he observes that "a lecturer should appear easy and collected, undaunted and unconcerned, his thoughts about him, and his mind clear and free for the contemplation and description of his subject."

In the autumn of 1813 Sir Humphry Davy left England for an extended tour through France, Italy and Switzerland, taking Faraday with him as assistant and amanuensis. This journey, which lasted about eighteen months, appears to have been the only occasion on which Faraday left England for any length of time, and it undoubtedly exercised a great influence on his future life. The travellers carried chemical apparatus with them, visited a large number of foreign chemists, and themselves experimented on the novel problems laid before them. They experimented with the newly discovered element, iodine, with which Ampère provided them, and of course prepared the explosive nitrogen iodine ; they visited Chevreul's laboratory, and attended a lecture by Gay-Lussac. Leaving Paris they drove across the Alps into Italy ; in Genoa they studied the electrical discharge from the torpedo fish, and spent some time in Florence burning diamond with the aid of the great burning-glass in the Accademia

del Cimento ; they visited Vesuvius, made the acquaintance of Volta, and Faraday made copious notes on the firefly and the glow-worm. They collected the natural inflammable gas at Pietra Mala, and identified it as methane in the laboratory of the Florentine Academy.

This lengthy journey, much of it in a country with which England was at war, must have been of inestimable benefit to Faraday ; he acquired some acquaintance with the outside world, and the insularity and indeed petulance which he occasionally displayed in his letters concerning the manners and customs of people with whose language he was unacquainted reveal his need for the wider experience thus afforded him. He saw the commanding position which Davy's genius as an experimental philosopher had acquired for him in European science, and, what was possibly of even more permanent importance, he had occasion to realise that the homage deservedly paid to his great master had led, perhaps, to some deterioration in those personal qualities which might be expected to accompany intellectual eminence.

In May, 1815, Faraday recommenced work at the Royal Institution, and shortly afterwards took possession of living apartments in this building. It must be remembered that this period was one of extraordinary interest in connection with chemical science. The sound experimental work of the previous century had freed the natural philosopher from the mystical and metaphysical trammels imposed by the alchemists, and had just led, through the work of Lavoisier, to an appreciation of the fact that quantitative measurements of weights and volumes had become the basis of an imminent great development in chemistry. Shortly before Davy had overthrown Lavoisier's view that oxygen was the acid-forming element, had shown that hydrogen chloride contains no oxygen, and had proved that "oxymuriatic acid" was an elementary substance which he called chlorine ; he had displaced caustic soda and caustic potash from their position as elements, and isolated from them the elementary metals sodium and potassium. Dalton had just enunciated the atomic theory, and Avogadro had stated his famous hypothesis that equal volumes of gases contain the same number of molecules under similar conditions of temperature and pressure ; both these fundamental statements of principle were destined to survive to the present day as logical deductions from experimental observation. The next few years were to see the popularising of chemical science by the introduction of Davy's safety lamp for use in coal mines, an invention which was probably greater than any other asset in determining the increasing industrial activities of this country.

This was the atmosphere in which Faraday found himself when he made his permanent home at the Royal Institution in 1815 : his publications of the succeeding few years show that he occupied himself busily in expanding his knowledge of science and in developing his remarkable talents as an experimenter.

Faraday's first contribution to chemical knowledge was a very modest one, and consisted in the examination of an Italian lime of volcanic origin; this was published in 1816, and was followed by some comments by Humphry Davy. His next essay was more ambitious. In 1816 the Professor of Mineralogy at Cambridge, E. D. Clarke, published a paper on the uses of the oxy-hydrogen blowpipe, an instrument which had been introduced by the American chemist, Robert Hare, in 1802. But whilst Hare fed hydrogen and oxygen separately into the blowpipe, Clarke proposed actually to use a mixture of the two gases in the requisite proportion; this involved the introduction of some device for preventing the flame from striking back and causing the explosion of the mixed gases in the reservoir. At this time Davy had perfected his safety lamp for use in the coal mines, and during this work had been led to reflect upon the various ways in which flame could be prevented from travelling through a body of inflammable gas; at Davy's suggestion Clarke caused the mixture of hydrogen and oxygen to pass through a short capillary of glass before entering the blowpipe. The explosion wave was extinguished by the cold walls of the capillary, and thus the risk of the explosion of the reservoir of gas was diminished; the risk was not entirely avoided, for Henry Gunning, in his "Reminiscences of Cambridge," notes the dangerous character of the oxy-hydrogen blowpipe as used by Professor Clarke, who was a somewhat eccentric and superficial enthusiast. At all events, Clarke succeeded in volatilising gold and in burning diamond with his blowpipe, and in 1817 Faraday published a note describing the repetition and extension of Clarke's results; it will be recognised that no little experimental skill had to be exercised in order to avoid the occurrence of a disastrous explosion. Shortly after, Faraday described an apparatus in which Davy's experiment of burning diamond can be performed in an enclosed space; the diamond is carried in a platinum capsule suspended in a glass globe filled with oxygen, and a jet of hydrogen, ignited by an electric spark, is used to heat the diamond to its ignition temperature.

Faraday's earlier papers were of the nature of short notes, and were published in the "Quarterly Journal of Science"; this was the organ of the Royal Institution, and had been started by Brande in 1816. Faraday's first paper in the "Philosophical Transactions" of the Royal Society appeared in 1821, and described the discovery and properties of hexachloroethane,  $\text{C}_2\text{Cl}_6$ , and its conversion into tetrachloroethylene,  $\text{C}_2\text{Cl}_4$ . Six months later he described and analysed another compound of carbon and chlorine, which Dr. Hugo Muller showed later to be hexachlorobenzene,  $\text{C}_6\text{Cl}_6$ , by a curious coincidence Faraday thus had a simple derivative of benzene in his hands several years before he discovered benzene itself.

It is remarkable that in these papers, and in their author's other



incursions into organic chemistry, no trace is found of a kind of mysticism which attended the treatment of carbon compounds almost until the middle of the nineteenth century. Lavoisier had shown that the majority of chemical substances produced as the result of animal or vegetable life contain carbon, and we still retain the name organic as descriptive of the carbon compounds. About 1760 the French naturalist, Buffon, stated that "there exists a living organic substance, universally distributed throughout all animal or vegetable substances, which serves equally for the nutrition, for the growth and for the reproduction of animals and vegetables." Even in 1849 Berzelius wrote that "the elements seem to obey quite other laws in living nature than in inorganic nature; the products which result from the reciprocal action of the elements thus differ in the two cases. If we could succeed in learning the cause of this difference we should hold the key to the theory of organic chemistry; but this theory is so well hid that we have no hope of discovering it." The same idea of the existence of a vital force as provocative of chemical changes in living matter is common to these two writers, separated by nearly a century. The hexachloroethane and the *tert.* chloroethylene were typical organic compounds; they were produced from ethylene, which in turn had been prepared from alcohol obtained by the fermentation of sugar. It is characteristic of Faraday's broad outlook upon chemistry that he should have dealt with organic compounds as subject to the same laws as govern chemical substances in general; in this modernity of conception he anticipated many of his successors.

Whilst this work was in progress Faraday was engaged in an investigation of the alloys of steel in conjunction with James Stodart; this had for its object the improvement of steel intended for the manufacture of cutting instruments and the diminution of the tendency to rust. A large number of new alloys were prepared and studied; some, such as those with platinum, had little tendency to rust, those with rhodium could be forged and tempered, and the silver-steel alloys were used for some time for the manufacture of such articles as fenders. Although Faraday occasionally presented his friends with razors forged from certain of his new alloys the work found no considerable technical applications; the modern extensive use of nickel-steel and chromium-steel, both of which Faraday prepared, suggests that the work was in advance of the needs of the times.

Another piece of work undertaken in 1822 led to results of far-reaching importance. Humphry Davy had shown that the supposed solid chlorine obtained by cooling moist chlorine is really a hydrate of this element; Faraday determined the composition of this unstable compound as, roughly,  $\text{Cl}_2, 10\text{H}_2\text{O}$ , but the exact composition is not yet known. On sealing the substance up in an inverted V-shaped tube, and warming the arm containing the chlorine hydrate, Faraday

observed that chlorine was given off, and became condensed to a yellow liquid in the empty arm; the hydrate had decomposed and the evolved chlorine had been liquefied by the pressure set up during its liberation. On cooling the arm containing the liquid chlorine to  $0^{\circ}\text{C}$ . and then opening the tube, part of the chlorine boiled off and the remainder became, in consequence, so cooled that it remained liquid under atmospheric pressure. Faraday estimated that the temperature so attained must have been lower than  $-40^{\circ}\text{F}$ ., and, as we now know, it is about  $-47^{\circ}\text{F}$ . He also found that chlorine could be liquefied at ordinary temperatures by four or five atmospheres pressure. The novel device of liquefying a gas by taking advantage of the pressure set up in a closed vessel by liberating the gas in a closed vessel was clearly capable of wide application, and its inventor immediately used it for the liquefaction of sulphur dioxide, hydrogen sulphide, chlorine dioxide, nitrous oxide, cyanogen, ammonia and hydrogen chloride. His interest in the subject aroused, he proceeded to liquefy a number of more refractory gases by cooling them under pressure in a bath of solid carbon dioxide and ether, and also succeeded in converting hydrogen bromide, hydrogen iodide, sulphur dioxide, hydrogen sulphide, nitrous oxide, ammonia and others into crystalline solids. The systematic study of the liquefaction of gases initiated by Faraday provided the foundation for much of the most brilliant work done within these walls by another great experimental genius, the late Sir James Dewar.

We now arrive, in this brief survey of Faraday's chemical work, at the moment of that important discovery which laid the foundation of more than one-half of modern organic chemistry and of one of the most important branches of chemical industry; this was the discovery of benzene which was announced to the Royal Society on June 16, 1825.

Early in the last century the Portable Gas Company was engaged in making illuminating gas by dropping whale or cod oil into a furnace maintained at a red heat; the inflammable gas produced by this process of destructive distillation was subjected to a pressure of about thirty atmospheres and stored in portable vessels. These latter were then transported to private houses and other buildings, and the gaseous contents burnt for illuminating purposes. During the process of compression a liquid was deposited, each 1,000 cubic feet of gas yielding nearly a gallon of this oil. Faraday subjected this condensed liquid to careful examination, and separated from it a compound of carbon and hydrogen which he termed bicarburet of hydrogen; he made a detailed study of this substance, and the analytical results which he obtained, translated into the modern nomenclature, give its molecular composition as  $\text{C}_6\text{H}_6$ .

The memoir in which Faraday describes the isolation of this hydrocarbon is written in very simple language, but it reveals throughout the handiwork of a genius in experimentation and of an

unrivalled master in the interpretation of experimental results. Thus, at this early date, and with the very modest appliances at his hand, the experimenter separated benzene in a state of purity from a very complex mixture; he found that it solidified on cooling, and gave its melting point as  $5.5^{\circ}\text{C}$ ., the correct melting-point being  $5.41^{\circ}$ . He determined the composition of the hydrocarbon by a method so ingenious that it might well tax the skill of the modern worker. He evaporated the hydrocarbon into a known volume of oxygen, noted the increase in gaseous volume, exploded the mixture in the endiometer and noted the diminution in volume, then treated with caustic potash solution and observed the further diminution in volume due to the removal of the carbon dioxide. The data thus obtained gave the proportion of carbon to hydrogen, and also the density of benzene vapour as compared with hydrogen as the standard; Faraday hence calculated the vapour density as 39, which is the correct value. This exhibition of real mathematical power as a mode of unravelling a complicated skein of quantitative data was followed by a profound study of the chemical behaviour of the new substance. Faraday noted that chlorine is without action on benzene in the absence of sunlight, but that when the mixture is exposed to sunlight vigorous action occurs, with evolution of hydrogen chloride; he succeeded in separating the solid chlorination product, obviously p-dichlorobenzene, from the liquid residue containing the o-isomeride. This was the first occasion on which the catalytic activity of sunlight in promoting the action of halogens on the aromatic hydrocarbons had been observed, and it is perhaps superfluous to remark that this particular aspect of catalytic activity is still growing in importance and is still a subject for scientific study. Many other points in this memoir of Faraday's might well call for distinction, but it will suffice to recall the comment passed upon the paper by Berzelius: "One of the most important chemical investigations which has enriched chemistry during 1825 is without doubt that of Faraday on the oily compounds of carbon and hydrogen obtained by compressing the gases obtained by the decomposition of fatty oils." The great Swedish chemist, himself the intellectual giant of the quantitative chemistry of his day, was impressed less by the new facts recorded than by the consummate art exercised in their elicitation and by the conviction that a new epoch had dawned in organic chemistry.

The bicarburet of hydrogen which Faraday separated from the gas obtained by the destructive heating of an animal oil was prepared by an entirely different means some ten years later. Mitscherlich obtained it in 1834 by distilling benzoic acid with lime, and proposed to give it the name benzin because of its relation to benzoic acid, which in turn derived its name from its original source, gum benzoin; Liebig objected to this name and proposed that it should be named benzol. Liebig's statement, made in 1834, that benzol could be obtained from coal, is possibly based on a misreading of

Faraday's paper in which he states that he had not been able to obtain it from coal-tar. The presence of benzol in coal-tar seems to have been first noted by John Leigh in 1824, and this observation was confirmed by Höfmann in 1845; in 1849 Mansfield was manufacturing benzol on a factory scale from coal-tar, and indeed lost his life in 1856 as the result of a fire which occurred whilst he was preparing the compound. The name benzol still survives as descriptive of the technical product, but the chemical name of the substance has now become benzene.

Benzene is the first member of a long series of compounds of carbon and hydrogen, the so-called aromatic hydrocarbons, which are closely related in chemical constitution and chemical behaviour. The second member of the series is toluene,  $C_7H_8$ , which was discovered by Pelletier and Walter in 1837, and is also separated in large quantities from coal-tar. Before discussing the modern importance of this particular series of aromatic hydrocarbons it may be well to refer to others with which Faraday was closely associated.

The hydrocarbon naphthalene was observed as a crystalline deposit in an apparatus used by Garden in 1819 for the distillation of coal-tar; its separation from coal-tar was described by John Kidd, the Professor of Chemistry at Oxford, in January, 1820. The chemical composition of naphthalene was determined by Faraday early in 1826; Faraday prepared the two isomeric derivatives, now known as the naphthalene  $\alpha$ - and  $\beta$ -sulphonic acids, and contributed further particulars concerning the behaviour of this hydrocarbon. The interest aroused in the components of coal-tar by Faraday's remarkable work on benzene and naphthalene led to a rapid increase in our knowledge of the composition of this raw material. In 1832 Dumas and Laurent separated anthracene from it, and, up to the present time, some thirty aromatic hydrocarbons, and more than that number of other aromatic compounds, have been extracted from this product of the distillation of coal.

It is worth while, if merely as an object lesson exhibiting the vast influence which can be exerted on the world's affairs by some originally modest piece of scientific research, to consider the scope and magnitude of the progress made as a result of Faraday's discovery of benzene one hundred years ago.

The whole of the great coal-tar colour industry sprang from Faraday's study of coal-tar. In 1856 the late Sir W. H. Perkin made the first coal-tar colour, Perkin's Mauve, from coal-tar benzene; and at the great Exhibition of 1862 a large number of such artificial colouring matters were displayed. So rapid had been the progress made during half a dozen years that in 1862 Hofmann was able to write as follows concerning benzene: "For years the newly discovered compound could claim scientific interest only. In this investigation, as indeed throughout the whole series of his immortal researches, Faraday's object was the elaboration of truth for its own

intrinsic value and beauty ; and in the same spirit has the work been continued by those who, after Faraday, engaged in the further scientific examination of the subject. Nobody, in those early days of benzol, when the substance simply existed as a laboratory curiosity, dreamed of the brilliant career looming in the distance for this body, nor of the marvellous transformations it was destined to undergo." But since the early days when Hofmann was moved to use these words the development of coal-tar colour manufacture has proceeded with progressive rapidity : the number of coal-tar colours now recognized as of technical value is of the order of 1200. Whilst the earlier artificial dyestuffs, although brilliant in colour, were often fugitive to light or to washing, we are now in possession of coal-tar colours which are more fast to light and to washing than indigo, madder, or any of the stable dyestuffs known to our ancestors. Many of the newer aromatic artificial dyes persist even when the fabric on which they are deposited has rotted away. The late Lord Playfair, and many other chemists, saw that the coal-tar colour industry was likely to influence in a remarkable manner the industrial fortunes of Great Britain. Hofmann put this view forward in 1862 in a remarkable passage : " For, if coal be destined sooner or later to take the place, as the primary source of colour, all the costly dyewoods hitherto consumed in the ornamentation of textile fabrics ; if this singular chemical revolution, so far from being at all remote, is at this moment in the very act and process of gradual accomplishment are we not on the eve of profound modifications in the commercial relations between the great colour-consuming and colour-producing regions of the globe ? Eventualities, which it would be presumptuous to predict as certain, it may be permissible to forecast as probable ; and there is fair reason to believe it probable that, before the period of another decennial Exhibition shall arrive, England will have learned to depend, for the materials of the colours she so largely employs, mainly, if not wholly, on her fossil stores. Indeed, to the chemical mind it cannot be doubtful that in the coal beneath her feet lie waiting to be drawn forth, even as the statue lies waiting in the quarry, the fossil equivalents of the long series of costly dye materials for which she has hitherto remained the tributary of foreign climes. Instead of disbursing her annual millions for these substances, England will, beyond question, at no distant date become herself the greatest colour-producing country in the world ; nay, by the strangest of revolutions, she may ere long send her coal-derived blues to indigo-growing India, her tar-distilled crimsons to cochineal-producing Mexico, and her fossil substitutes for quercitron and safflower to China, Japan, and the other countries whence these articles are now derived."

This pronouncement of Hofmann is interesting in that it involves two propositions, the one correct and the other incorrect. The instinct and wide experience of the chemist told him, and told him

correctly, that the coal-tar dyes were destined largely to replace the vegetable colouring matters and to provide the textile manufacturer with increased opportunities for the production of new effects; but when he took for granted that the new discovery would find vigorous commercial development in the country of its birth he was forming an opinion on a subject less his own than chemical science. Within a few years this country was exporting coal-tar to Germany for dyestuff manufacture, and, whilst artificial colour manufacture languished in this country, Germany forged ahead and soon dominated all others in the new industry. Indigo-planting and indigo preparation did indeed dwindle into insignificance, largely because no concerted effort was made to apply scientific methods to the improvement of methods which had remained unchanged for perhaps a thousand years; but it was Germany who exported artificial or coal-tar indigo to India and not Great Britain.

It has just been hinted that scientific cultivation and scientific methods of separation might have enabled natural indigo to hold its own against artificial indigo produced from the components of coal-tar; there is indeed solid foundation for the belief that natural indigo, had its production not been woefully mismanaged, would never have been supplanted by the artificial material. It would appear likely that the percentage of colouring matter yielded by the indigo plant might be greatly increased by scientific breeding and by improved methods of extracting the colour: the percentage of sugar obtained from the sugar beet by judicious selection of seed and careful development of methods of extraction was raised from little more than 5 per cent. to about 20 per cent. on the weight of the beet. Furthermore, and for reasons which need not now be discussed, it seems clear that natural indigo is of distinctly greater value as a dyestuff than the artificial product. These facts were realised by the Government of India many years ago; a scheme of research work was launched, financed by the State, and notable advances were made in the manufacture of natural indigo. But at the moment when it had become clear that indigo planting could be given a new and profitable lease of life the Indian Government, apparently from motives of economy, abandoned the research scheme; the considerable expenditure which had been incurred thus represented, for all practical purposes, an extravagant waste of money. It seems at first sight irrational to spend a large sum of money in proving the truth of a scientific forecast as to how a particular scientific industry can be made to flourish and to abandon the project at the moment of fructification; at the same time, the fact that this remarkable method of procedure is the standard method adopted by British Governments would seem to indicate that it has a sound economic basis.

But whilst little or nothing was done to stimulate the cheap production of natural indigo, neither effort or money was spared in the attempt to manufacture coal-tar indigo in the German colour

works; it has been stated that £2,000,000 were spent on chemical research and technical development before synthetic indigo was put upon the market. The vast amount of chemical and technical experience gained during this great enterprise did not lead to the production of indigo alone; many compounds closely allied to indigo and possessing value as dyestuffs were also made. Included among these is the traditional Tyrian purple, which is contained in the secretions of a small marine snail.

Again, the competition amongst coal-tar dyestuff manufacturers led to new developments in connection with the manufacture of entirely novel dyes of like stability to indigo, although belonging to entirely different classes of chemical compounds. Many of these, grouped together as the so-called "vat-dyestuffs," are derivatives of the hydrocarbon anthracene which has been previously mentioned; they can be produced from anthracene separated from coal-tar. But coal-tar anthracene is costly, whilst the two hydrocarbons with which Faraday was so closely associated, benzene and naphthalene, can be extracted from coal-tar in large quantities at but little expense. As an illustration of the thoroughness with which chemical skill has been applied to the solution of the economic problems which arise in the manufacture of artificial colouring matters may be quoted the fact that the cheap raw materials, benzene and naphthalene, can now be used instead of anthracene itself in the manufacture of the dyestuffs relating to anthracene. Naphthalene can be partially burnt in the air so as to yield phthalic acid; this phthalic acid can be caused to condense with benzene to give anthraquinone. The anthraquinone thus manufactured can be used to replace that previously obtained from the costly anthracene, and can be utilised in the manufacture of the better-class vat-dyestuffs.

Whilst the manufacture of coal-tar dyes grew to vast dimensions owing to wise development and exploitation, other industries and fields of knowledge also benefited. In course of time it was found that Faraday's benzene was the starting material for many aromatic substances of use in medicine, in photography and in many other arts. Furthermore, the coal-tar hydrocarbons, benzene and toluene, are the raw materials from which the high explosives, picric acid and trinitrotoluene, are manufactured. At the outbreak of the recent war, no picric acid was being made from benzene, and no trinitrotoluene had ever been made on a large scale in this country. This was of course well realised on the Continent; to what extent the known unpreparedness of Great Britain for the manufacture of the staple high explosives was a factor in precipitating war cannot now be ascertained.

The set of great industries involved in the manufacture of artificial dyestuffs, pharmaceutical products, and military and naval high explosives are thus closely allied. Faraday's discovery of benzene and its analogues is also important in connection with liquid fuel

used in the ordinary internal combustion engine. Certain of the naturally occurring petroleum contain large proportions of aromatic hydrocarbons, such as benzene, and the fact that a petroleum from Borneo containing about 20 per cent. of benzene and toluene was available in 1914 was a very material relief to the difficult situation created by the impossibility of immediately preparing large quantities of raw materials from coal-tar for the manufacture of high explosives. Benzene and toluene from coal-tar are now largely used for blending with petrol from overseas and for improving its efficiency as a fuel.

In the year 1825 Faraday undertook, at the request of the Council of the Royal Society, a lengthy and laborious experimental study of the manufacture of optical glass: the investigation extended over four years, and was fruitful in that it provided a great deal of accurate and precise data as to the conditions to be desired or to be avoided in the making of glass for optical instruments. The notable positive result of the work was the discovery of the so-called heavy glass, which consists largely of a lead borosilicate and has very high refractive power. The expenses incurred in carrying out this work were amongst the objects of a violent attack levelled against the President and Council of the Royal Society in 1830 by Sir James South. The "heavy glass" was destined later to serve in Faraday's discovery in 1845 of the rotation of the plane of polarisation of light when passed through a transparent medium in a strong magnetic field; this property, that of magnetic rotatory power, took its place amongst the important physical constants of chemical substances as a result of the work of the late Sir W. H. Perkin.

Yet another brilliant piece of Faraday's experimental chemical work remains to be mentioned. He had noted that films of beaten gold of some  $1/280,000$ th of an inch in thickness are translucent, and that the transmitted light is green in colour; from this observation he was led to study the transmitted colour of still thinner films of gold and other metals, and to the conclusion that glass, fused with the addition of a trace of a gold salt, owes its ruby colour to the diffusion throughout the mass of minutely divided gold. The reduction of metallic gold in aqueous solution also engaged his attention, and he concluded that the bright red-coloured solutions thus obtained owed their colour to the diffusion of minute particles of metallic gold throughout the liquid. These coloured and apparent solutions of metallic gold in water are very stable; their study by Faraday in 1857 was an obvious prelude to the classical studies of colloidal solutions published by Thomas Graham, the Master of the Mint, in 1861.

So far I have dwelt, perhaps with too much insistence, on Faraday's pre-eminence as an experimenter, and, possibly again in too accentuated a manner, with the world-extended influence of his



chemical work on the subsequent history of our planet. Such possible defects call for an apology. Faraday came forward as an experimental genius at a time when the chemist was forced to work with the aid only of ordinary domestic appliances, and when he had to make for himself every item of the apparatus which he desired to use. His "Chemical Manipulation," published in 1829, provides a fund of information concerning details of chemical experimentation of which the chemical student of to-day is entirely ignorant. We have progressed so far in our experimental study of chemical phenomena that the investigator is now but little dependent on his own manipulative skill, and has become largely subservient to the ingenuity of the scientific instrument maker. Again, an apparently non-utilitarian experimental discovery made in one generation seems naturally to become the corner-stone of some gigantic industrial development in the next decade. A perusal of Faraday's experimental work furnishes ample material in support of this thesis: and, to come nearer to the present day, many of those present to-night had the privilege of witnessing those fundamental experiments on the liquefaction of gases, shown in this theatre by Sir James Dewar, which have become the foundation of great industries.

It would be a mistake to attempt to measure the achievements of Faraday on a scale derived from a consideration of the immediate material benefits to the world which have accrued from his work. Probably no man, with the possible exception of Newton, has ever exercised throughout a century such a persistent directive impulse to the activities of a huge body of scientific workers. This is the more strange in that Faraday was essentially a solitary worker; the long list of his published papers includes but two in which he is named as a joint author. It would almost seem that the man was endowed with such consummate skill as an experimenter that any collaborator of his day would have impeded the progress of a joint investigation. It might perhaps have been anticipated that one so much accustomed to work alone, and as a pioneer far ahead of most of his contemporaries, would have tended towards narrow specialisation and have gradually lost interest in other branches of scientific activity by reason of intense cultivation of his own field of investigation. Some justification for such an expectation may be sought in the fact that although he was the first Secretary of the Athenæum Club he resigned the position after one year of office, and that he declined nomination to the Presidency of the Royal Society on the ground that it would impede his experimental work. But the lengthy correspondence of Faraday with Schönbein, Liebig, Whewell, Wheatstone, Agassiz, Dumas, Wollaston, Herschel, de la Rive, Gay-Lussac, and a host of other great contemporaneous scientific men, shows that his interests were widespread, and that he bore always in mind his primary concern for the advancement of natural philosophy as a whole. One of the most acute judges of his fellow-men, the Count

Camillo Cavour, records an appreciation which is worthy of quotation ; he found Faraday "without a waistcoat, in a ragged old coat, looking for all the world like a sixteenth-century savant. But one can see that he has great rapidity of perception, and quickness of decision—two qualities which lead almost instinctively to these great discoveries. There is not a scrap of scientific conceit about him."

In this conservation of a wide scientific interest, so difficult for an isolated worker, the nature of Faraday's duties in the Royal Institution must have played a great part. One of his major tasks consisted in expounding the results of current scientific progress to a cultured though not a specialist audience ; his sense of responsibility towards that audience led him so to train his powers that he became the most efficient popular exponent of science of his day. His lectures to children on the chemical history of a candle show that he was an unrivalled master of lucidity of exposition and a genius in the device of simple but convincing illustrations.

It must not, however, be imagined that Faraday confined himself to the discovery and exact statement of experimental facts without thought for their theoretical significance. His respect for a bold and far-reaching generalisation, put forward as a mathematical interpretation of facts—and this is what is meant by a theory—is expressed in many of his writings. He begins one of his papers with the following passage : "That wonderful production of the human mind, the undulatory theory of light, with the phenomena for which it strives to account, seems to me, who am only an experimentalist, to stand midway between what we may conceive to be the coarser mechanical actions of matter, with their explanatory philosophy, and that other branch which includes, or should include, the physical idea of forces acting at a distance ; and admitting for the time the existence of the ether, I have often struggled to perceive how far that medium might account for or mingle with such actions generally, and to what extent experimental trials might be devised, which, with their results and consequences, might contradict, confirm, enlarge, or modify the ideas we form of it, always with the hope that the corrected or instructed idea would approach more and more to the truth of nature, and in the fulness of time coincide with it." The literature of science may be searched in vain for a more sympathetic and a more accurate definition of the relation which should exist between the pure experimenter and the mathematical interpreter of the observed facts : and because Faraday was both. Clerk Maxwell, who was the first to translate Faraday's brilliant conceptions into mathematical language, and to apply to them all the powerful methods of the mathematical workshop, observed that : "The way in which Faraday made use of his idea of lines of force—shows him to have been in reality a mathematician of a very high order—one from whom the mathematicians of the future may derive valuable and fertile methods." This is the deliberate opinion of one who was

not given to exaggeration, and who, in the course of a short life, contributed more perhaps than any other to the development of mathematical physics in the Victorian period. That Clerk Maxwell's judgment was sound is obvious to all who have had occasion to study the remarkable series of experimental researches in electricity published by Faraday between 1831 and 1860; early in these classical investigations Faraday succeeded in forming very clear ideas concerning the manner in which an electric current operates in the decomposition of water or of salts in solution. He showed that when water is electrolysed the quantity decomposed is exactly proportional to the quantity of electric energy which has passed, and that the products of the decomposition can be collected and measured "with such accuracy as to afford a very excellent and valuable measurer of the electricity concerned in their evolution." He showed further that in all cases the quantity of chemical decomposition is exactly proportional to the quantity of electricity which has passed through the electrolyte, and that a given quantity of electric energy liberates chemically equivalent amounts of the metals during the electrolysis of metallic salts. In this way Faraday was able to determine a series of numbers representing the electrochemical equivalent of the elements, and to show that the electrochemical equivalent is the same as the chemical equivalent. It remained for a later worker, Sir Edward Frankland, to formulate the conception of valency, to point out that the true atomic weight of an element, divided by the valency, gives the chemical equivalent, and so to pave the way for securing the atomic theory in its present impregnable position. The work of Faraday on electrolysis was one of the essential steps taken during the nineteenth century to realise what Newton foresaw when he remarked: "It seems probable to me, that God in the beginning formed matter in solid, massy, hard, impenetrable movable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as must conduce to the end for which He formed them; and that these primitive particles, being solids, are incomparably harder than any porous body compounded of them, even so hard as never to wear or break in pieces; no ordinary power being able to divide what God Himself made one in the first creation."

But still more far-reaching consequences resulted from Faraday's electrochemical work: he often expressed his conviction that the forces termed chemical affinity and electricity are one and the same, and he had been led to associate a definite quantity of electricity with the liberation of the atomic unit of an element from combination. There must thus exist a definite minimum unit of electricity; and, as Helmholtz indicated more definitely in 1880, not only matter, but also electricity itself has an atomic structure. The discoveries of the last thirty years, which have resulted in the isolation of the atom of negative electricity, the electron, and the identification of

the atom of positive electricity with the positively charged hydrogen atom, are the logical outcome of the work of Faraday.

To the chemist the discussion, applications and extension of Faraday's electrochemical conceptions have been a fruitful source of inspiration and progress for nearly a century; as time passes on those conceptions are seen to increase continually in fundamental significance. It cannot be doubted that when the second centenary of the discovery of benzene is honoured in this theatre a hundred years hence my successor will be able to point to consequences, still more fundamental and far-reaching, of the work and thought of perhaps the greatest experimental genius the world has ever seen.

[W. J. P.]

Friday, January 29, 1926.

SIDNEY G. BROWN, F.R.S. M.I.E.E., Manager, in the Chair.

SIR WILLIAM B. HARDY, F.R.S., Fellow and Tutor of Gonville and Caius College, Cambridge.

### Films.

THE title of this discourse is perhaps misleading. It has, I find, suggested to my friends a popular form of entertainment. Let me hasten to set this right. I shall have nothing to say about the cinema! My subject is something quite different—namely, those thin films of matter familiar to all in the form of soap bubbles or lubricating films of oil.

The subject is of great scientific interest. You all of you know of the three states in which matter can exist—solid, fluid and gas or vapour. These films are no less than a fourth state, because, choose what physical constant we may, it will have a different value for any particular kind of matter in this state to what it has in any of those other states which are more easily apprehended by the senses.

Life itself depends upon this fourth state of matter. There is a film spread over the surface of each living cell which seems to control the passage of substances into or out of the cell. This film is actively maintained by the expenditure of energy on the part of the cell. The new technique of microdissection, by which living cells so small as to be almost or quite invisible can be dissected, has increased our knowledge of this surface film. If it be punctured at one place, the living matter in the neighbourhood of the puncture becomes curdled in appearance and dies, but the membrane grows in at the back of this dead substance cutting it off from the rest of the cell. This is the fundamental surgery of life.

I cannot hope to do more in one hour than deal in haphazard fashion with this vast subject. I propose to begin with an experiment which, in spite of its simplicity, shows how ubiquitous films are, and how our most elementary impressions of the external world depend upon them.

Take, for example, smoothness. It is not a property of solid matter in mass, but of this fourth state of matter. A tea-cup has the delicate velvety feel of a polished surface; but neither porcelain nor ware is really smooth in that sense. Their surface, like that of all other naturally occurring surfaces, is covered by a film of greasy

matter, which can come from the atmosphere or from the "clean" cloth with which the object has been dried. If that film be removed the surface feels harsh and rough because, to use the engineer's phrase, one's finger-tips, if they are freshly washed, seize to it.

It is not possible here and now to remove the film. The necessary procedure would take too long, and in any case the film would quickly re-form in this atmosphere. I can, however, destroy its effectiveness by taking advantage of a curious property of water. That substance is not only not a lubricant for vitreous surfaces, but it is also an anti-lubricant in that it destroys the effect of the natural lubricating film. All I have to do, therefore, is thoroughly to wet the surfaces of the tea-cup and saucer, and the tea-cup ceases to slide in the saucer.

A tea-cup suggests a storm, and that suggests the curious power which oil has of smoothing the sea. The oil spreads over the surface of the water until the layer is only about the five-millionth of a millimetre in thickness. A figure of that kind is apt to mean little; I will therefore try to give you an impression of the minute quantity of oil needed in another way. In 1919 an oil ship was wrecked inside the Lizard. The oil-tanks were burst open and the oil rapidly escaped. There has been no sensible quantity of oil in the wreck for the last six years, yet sufficient still escapes to the surface of the sea to produce an obvious "smooth" for a mile or more to leeward. The effect of a film of oil of quite invisible thickness upon the sea is very real. A vessel labouring in a sea-way or running before a gale can, and does, find some measure of safety by streaming bags filled with oil to windward, and Pliny records how the oyster-fishers used oil to calm the surface of the sea so that they were more easily able to work.

It is obvious that the presence of this oil film cannot seriously modify the energy of great seas, say, a quarter of a mile from crest to crest; but when seas enter a "smooth" they change their character with dramatic suddenness. They lose their viciousness, and the moment they are in the "smooth" take the character of those relatively harmless undulations which do not break on to a vessel, but merely make her roll and pitch. The question how the oil film, so tenuous as to be of invisible thickness, curbs the seas is an interesting one, and the attempt to answer it will inevitably introduce us to the chief properties of films on water.

In the late nineties a most ingenious method of demonstrating the existence of films on water, and of controlling them for experimental purposes, was devised by a German lady, *Fräulein Pockels*. I think I may say without exaggeration that the immense advances in the knowledge of the structure and properties of this fourth state of matter which have been made during this century are based upon the simple experimental principles introduced by Miss Pockels. I propose now to make use of her method. Here is an oblong trough

of metal filled with water. On the surface of the water, quite invisible to you because it is even thinner than the invisible dead black portion of a soap film, there is a layer of greasy contamination. If I lay upon the trough a strip of glass or metal so that it touches and is wetted by the water, and move it along, I can compress the superficial film in front and expand it behind. Both processes are easily rendered visible by scattering lycopodium dust on the surface.

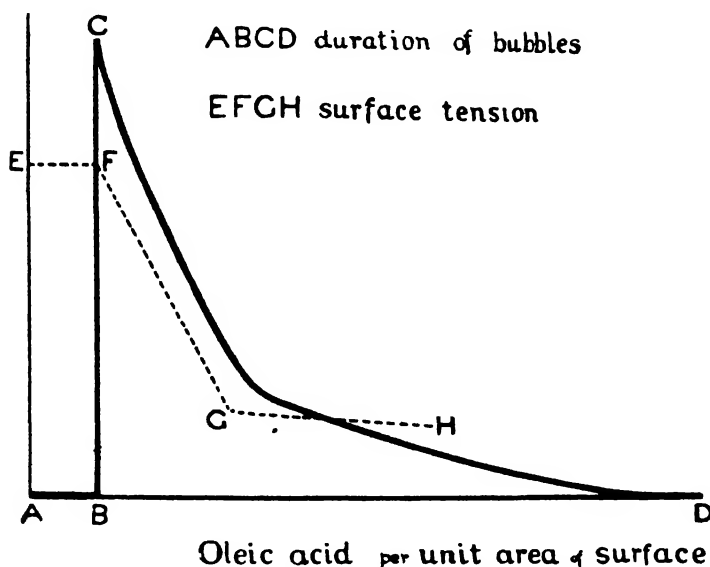
The capacity which these films have of expansion is easily shown by sweeping the natural film to one end, thus leaving a tolerably clean surface of water behind. Some lycopodium dust is now placed at one end and the surface touched with a platinum wire, the extreme tip of which has just been dipped into an oil. The dust particles are swept swiftly away in front of the advancing film of oil, although the film itself is absolutely invisible.

The film tends to spread, but the surface of the water in virtue of its surface tension tends to contract. It is this same surface tension which rounds up drops of fluid to spheres, or as near an approach to the spherical shape as other forces which may be operating, such as gravity, permit. There are therefore opposing influences: the tendency of the water to contract, opposed by the tendency of the film to expand, with the result that composite surfaces of oil and water have a surface tension less than that of pure water. Composite fluid surfaces have also an enhanced mechanical stability. When a ring of wire a few centimetres in diameter is withdrawn from clean water no film is formed across it, but when the surface of the water is coated with oil it acquires the property of forming free films, which may have an endurance comparable even with that of a soap bubble. In the figure the curve EFGH gives the surface tension plotted against the quantity of oleic acid per unit area of surface, and the curve ABCD gives the duration of bubbles which have been formed on the surface by allowing air to escape slowly and regularly from an orifice within the trough. It will be noticed that the bubbles are most stable when the film of contamination is just dense enough to begin to alter the surface tension, and that the bubbles have no stability when contamination is either vanishingly small or very great.

Do these properties of composite surfaces, namely, the lowered surface tension and the increased mechanical stability, explain the calming of the sea? In my opinion the answer is "No," but current doctrine would perhaps say "Yes." It has been pointed out that the special capacity of composite surfaces to resist extension and their mechanical stability, which is only another special aspect of the same thing, tends to prevent the inevitable expansion of the surface which occurs when a wave is formed. This has been held to be a sufficient explanation. I do not think it is, and for two reasons. The first is that the surface of the sea always is contaminated by something which lowers its surface tension and gives to it a remarkable measure

of mechanical stability. One of the most striking aspects of a heavy gale is the "windrows," which are due to the foam formed when a sea breaks being blown by the wind in long lines over the surface. Foam after all is no more than a collection of bubbles; obviously therefore these naturally formed bubbles have great stability.

The surface of the sea is already covered by a film of matter the nature of which must remain uncertain. Sometimes it is composed of substances, like saponin of vegetable origin, derived from the masses of seaweed flung upon the coast. Foam of this kind is remarkably stable. I have seen it on the day following an on-shore gale knee-deep in the hollows above Flamborough Head. The bruising and



shattering of seaweed is however a coastal happening and "windrows" are deep-sea phenomena.

The true explanation was, I think, furnished by Benjamin Franklin in 1773. His discussion is worth reading. It has the spacious dignity and charm which the hurry and specialisation of to-day have of necessity banished from scientific papers. He tells how he was at sea in 1757 with a convoy of 96 sail, the wind being very fresh, and how he noticed a "smooth" in the wake of two of the vessels. He enquired the cause of one of the officers and was told with some degree of contempt, it being a thing which every fool should know, that the "smooth" was due to the fact that the cook had just thrown greasy water over the side. In those days tallow



was used to coat the bottoms of vessels to keep them clear of growth, and Franklin also notes the "smoothness" in the wake of vessels which had been freshly tallowed.

Franklin's explanation is based entirely upon friction. The oil makes the sea so very smooth that the wind cannot "catch upon it." I confess Franklin's explanation did not appeal to me at first, but I believe he is right. The comparative safety of a "smooth" is due not to the fact that the seas in it are sensibly smaller than those outside of it, but to the fact that they have been deprived of their viciousness. Now the viciousness of a sea, the degree of danger it carries to the mariner, is measured by its instability. It is when the head of the sea topples over and becomes a mass of water moving with a high velocity that it is dangerous. Within the limits of a "smooth" produced by oil the seas cease to break, or to "crack" as Cornish fishermen say. The wind not only drives a sea forward by its horizontal pressure, but also draws the crest upwards by friction against the surface of the wave.

If the friction between the air and the water be greatly reduced, the wind fails to lift the crest of a wave to the point at which it is blown bodily over by the horizontal pressure. The wave then sinks down to a relatively harmless "swell."

The "catch" of the wind upon the waves is not however confined simply to a direct frictional pull, and here it is that the surface tension phenomena perhaps come in. It is easy to convince oneself that an oil film prevents the formation of ripples—that is, of the very smallest kind of wave. When there is no oil film a great wave carries countless ripples and wavelets each of which gives the wind a direct thrust on the surface. It is to the suppression of ripples and wavelets that the characteristic smooth appearance is due, and when they cease to be formed the chief "catch" of the wind upon the sea is lost.

[W. B. H.]

Friday, February 12, 1926.

SIR ERNEST MOON, K.C.B. K.C. LL.B., Manager and  
Vice-President, in the Chair.

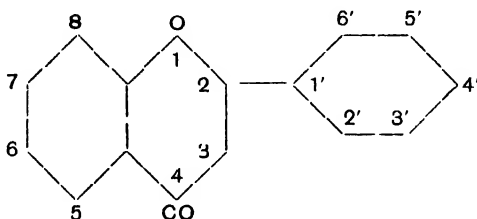
ROBERT ROBINSON, D.Sc. F.R.S., Professor of Organic Chemistry,  
University of Manchester.

### Chemistry of Red and Blue Colouring Matters of Flowers.

PRIOR to the work of Richard Willstätter, the publication of which began in 1913, there was a striking deficiency in our knowledge of the nature of the bright red and blue, violet, purple, mauve and magenta colours of flowers, fruits and blossoms. These water-soluble anthocyanin pigments occurring in the cell sap were already distinguished from the water-insoluble plastid pigments, such as carotin, xanthophyll and chlorophyll, which occur alongside protoplasmic bodies, and many of their superficial reactions were known. Glenard (1858), Senior (1878), Heise (1889), and Glan (1892) examined various imperfectly purified anthocyanins and found these to contain carbon, hydrogen and oxygen only: whilst Griffiths (1903) obtained the geranium pigment in a crystalline condition, and came to the same conclusion regarding its elementary composition. Moreover, the botanist Molisch showed in 1905 that in many cases the pigments exist in the living plant in a microcrystalline condition, and followed up this observation by demonstrating the crystallisability of several of these colouring matters on a small scale outside the plant. Molisch considered that the crystalline pigments contained sugar in a combined form, but when Grafe succeeded in reproducing Molisch's experiments on a larger scale with pelargonium petals, he failed to recognise that the crystalline colouring matter he had obtained was a glucoside. Willstätter and Everest (1913) examined anthocyanins in general, and the pigment of the cornflower in particular. They found that the anthocyanins are glucosides having both basic and acidic properties. The anthocyanin of the blue cornflower they called "cyanin," and showed that it exists in the plant as its potassium salt. It was, however, isolated by taking advantage of its power of forming compounds with acids rather than with alkalis. These salts—for example, potassium cyanin and cyanin chloride—could be crystallised, the latter with much the greater ease. The action of boiling 20 per cent. hydrochloric acid on cyanin chloride splits off the sugar groups and gives glucose (2 mols.) and cyanidin chloride,

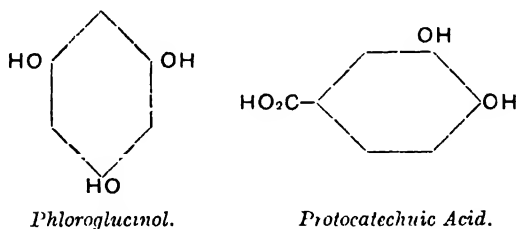
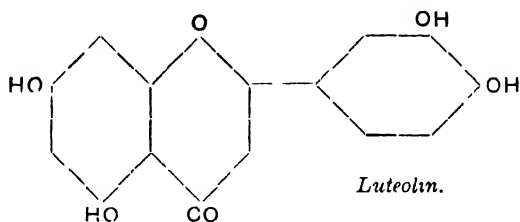
which crystallises from the solution. The name "anthocyanidin" is applied to all the sugar-free pigments which can be obtained by detaching sugar from the anthocyanins. Only in the case of the colouring matter of the skins of black grapes is the anthocyanin—namely, oenin—supposed to be accompanied in nature by the corresponding anthocyanidin—namely, oenidin. Anthocyanin chlorides are much more soluble in water, thus partaking of the character of the sugar contained in their molecules, than are the anthocyanidin chlorides. The latter are completely extracted from aqueous solution by amyl alcohol, whilst the anthocyanins are only removed to a certain extent, usually to a very small extent, by this solvent. Subsequent work showed that cyanin is contained in red as well as blue flowers, and the following figures give the percentage of the colouring matter in the dried petals: Blue cornflower, 0.75; deep violet-blue cornflower, 3.6; deep bordeaux cornflower, 13–14; deep red dahlia, 20; *Rosa gallica*, 2. About 50 per cent. of the amount present in deep red dahlia petals can be isolated in the following manner. The fresh flowers are extracted with acetic acid, methyl alcoholic hydrochloric acid, and  $1\frac{1}{2}$  volume of ether being then added. This precipitates the chloride, which is insoluble in ether, and the salt may then be separated and crystallised in the ordinary manner from a solution in 7 per cent hydrochloric acid. It should be added that this process is unusually straightforward owing to the high percentage of colouring matter in the flowers, a tribute to the effective work of the florists. Willstatter and Nolan, who prepared cyanin chloride from petals of *Rosa gallica*, showed that cyanin chloride had the composition  $C_{15}H_{11}O_5Cl$ . Willstatter and Bolton isolated the anthocyanin, pelargonin, from the scarlet pelargonium, and found that the sugar-free pigment, pelargonidin chloride, had the composition  $C_{15}H_{11}O_5Cl$ : whilst Willstatter and Mieg obtained delphinin from the wild purple larkspur (*Delphinium consolida*), and found that it could be degraded to delphinidin chloride,  $C_{15}H_{11}O_5Cl$ . Every anthocyanin pigment which has been closely examined up to the present time has been found to be derived from one of the three anthocyanidins already mentioned, and the variety of flower colours is due to what may be described as the various exterior fittings of the molecules, as well as to the nature of the sap. If the latter is acid the colour tends to be red, if it is neutral the flower may be violet or purple, and if it is alkaliescent the flower will be blue. Anthocyanins derived from pelargonidin occur in the scarlet *Pelargonium zonale*, the purple-red summer aster, the scarlet *salvia*, and in radishes. Cyanidin derivatives are very widespread, and have been detected in the cornflower, rose, dahlia, chrysanthemum, aster, peony, poppy, and in the fruits of the cherry, cranberry and sloe, as well as in many other flowers, fruits and berries. Delphinidin is obtained from the anthocyanins of grapes and bilberries, and of the flowers of delphinium, hollyhock, petunia, wild mallow and viola. It is obvious

that the problem of the molecular structure of the anthocyanins must be attacked by way of that of the simpler anthocyanidins, and in this matter conjectures confirmed by crucial experiments played a leading part. In the first place the analogy in composition between the anthocyanidins and the yellow plant colouring matters of the flavone and flavonol series could not be overlooked. Thanks to the labours of A. G. Perkin, von Kostanecki, and other chemists, we already possessed a knowledge not only of the wide distribution of these anthoxanthins in nature, but also of the details of their molecular structure. They are all of them derivatives of flavone,  $C_{15}H_{10}O_2$ , a compound which was synthesised by Kostanecki, and



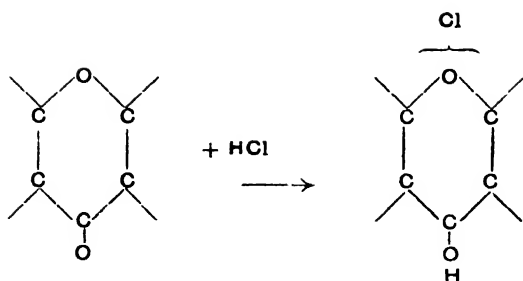
subsequently discovered by Muller to be the chief constituent of the farina of *Primula pulverulenta*. The other naturally occurring flavones have OH instead of H in several of the possible positions, and this substitution confers on them a weakly acidic character. It should be noticed that many of the hydroxylated flavones are weak bases and form readily decomposable salts with strong acids. We pass in review the established constitution of a few of the members of the group. Chrysin,  $C_{15}H_{10}O_4$ , from poplar buds has OH instead of H in positions 5 and 7; apigenin from parsley has the formula  $C_{15}H_{10}O_3$ , and the OH groups are in 5, 7 and 4'; luteolin from weld is  $C_{15}H_{10}O_6$ , and has OH groups in 5, 7, 3' and 4'. Scutellarein from *Scutellaria altissima* has its four OH groups in 5, 6, 7 and 4'. The flavones with an OH group in position 3 are called flavonols, and are more widely distributed than the flavones. Kämpferol,  $C_{15}H_{10}O_6$ , has OH groups in 3, 5, 7 and 4'; it can be obtained from *Delphinium consolida*. Quercetin,  $C_{15}H_{10}O_7$ , with OH groups in 3, 5, 7, 3' and 4', is found widespread in nature. Derivatives of it occur, for example, in the inner bark of *Quercus discolor* Ait., in the leaves of *Eucalyptus macrorhyncha*, in rue, capers, buckwheat, clover flowers, cotton flowers, wallflowers, horse-chestnut, etc. Myricetin,  $C_{15}H_{10}O_8$ , with OH groups in 3, 5, 7, 3', 4' and 5', is obtained from *Myrica nagi*, the ever-green box-myrtle of China, and other plants. All these flavones and flavonols have been artificially prepared in the laboratory, and, so far as is known, they all occur in the plant in combination with sugars. In order to appreciate the analogy in composition

between the flavones and anthocyanidins, it is merely necessary to note that luteolin combines with hydrochloric acid to form a hydrochloride which has the same empirical formula,  $C_{15}H_{11}O_6Cl$ , as cyanidin chloride. Now when luteolin is fused with caustic alkalis its molecule is destroyed, but not so completely that none of the fragments can be recognised. The middle ring of atoms is wholly broken up by this vigorous treatment, but the benzene rings to some extent withstand the strain. The products which can be isolated are called phloroglucinol and protocatechuic acid; they are substances which can be artificially prepared in several different ways, and the position which they occupy in the system of organic chemistry is perfectly well understood. The first indication that the hypothesis of a close relation between the flavones and the anthocyanidins is correct was the fact that when cyanidin chloride was fused with alkali it also yielded phloroglucinol and protocatechuic acid.

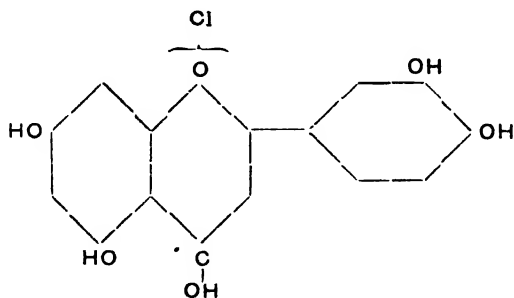


A second group of researches precedent to those of Willstätter and his collaborators was concerned with the basic character of non-nitrogenous carbon compounds containing oxygen. Many substances of this type exhibit a weak affinity for acids, but Collie, Werner, Baeyer, and others showed that quite stable so-called oxonium salts are formed by a group of compounds the molecules of which include a ring of five carbon atoms and an oxygen atom. Such a ring is contained in flavone and its derivatives.

In accordance with modern ideas the salt formation is represented by the above scheme, and the bracket between Cl and O is a symbol expressing the view that the chlorine atom on the one hand, and the rest of the molecule on the other, are electrically charged in opposite

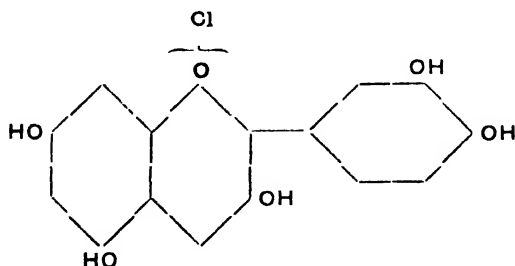


senses. It was then found that even more stable salts can be obtained by adopting such methods of synthesis as will rise to compounds in which the OH of the above formula is replaced by H. Oxonium bases of this type have been recently encountered that are strong enough to form stable acid carbonates. If now we consider what modification of the constitution of luteolin hydrochloride could supply an explanation of the nature of the isomeric cyanidin chloride,

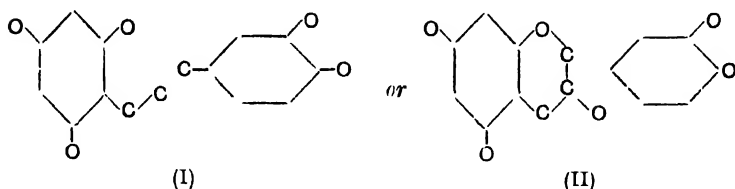


*Luteolin hydrochloride.*

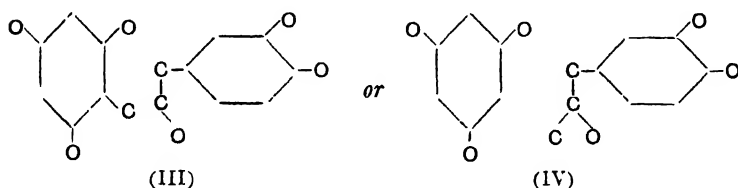
we perceive at once that the expression annexed demands serious consideration. Three independent syntheses of cyanidin chloride



have proved conclusively that this formula does, in fact, represent the constitution of the substance. In Willstätter's syntheses the bricks were



whilst in those which were performed in St. Andrews and Manchester the bricks were



Method III is the only convenient and general process.

Pelargonidin chloride differs from cyanidin chloride in that it lacks the OH group in position 3', whilst delphinidin chloride has OH groups in 3', 4' and 5', as well as in 3, 5 and 7. The former anthocyanidin has been artificially prepared by methods (II), (III) and (IV), and the latter by two variations of method (III). The nucleus common to the anthocyanidins we call conveniently "flavylium," and denote the position of attached groups by the numbering system already adopted for flavone. A large number of flavylium salts have been prepared in order to obtain information as to the influence of the position of OH groups on the properties of the substances.

(1) As the number of OH groups increases, the colour of acid solutions passes from nearly colourless, through yellow, orange and red, to bluish red.

(2) If there is an OR group in position 3, solutions of the salts are decolorised on dilution, and in most cases the colour is restored on the addition of acid.

(3) If there is an OH group in position 7, leaving positions 5 and 8 free, the salt may exhibit fluorescence in alcoholic solution.

(4) Only certain combinations of OH groups in at least four positions (two of which must be 3 and 4') confer on the salt the power of dissolving in aqueous sodium carbonate solution to a pure blue solution. Such combinations are : 3, 5, 7 and 4', and 3, 7, 8' and 4'.

(5) An intense colour reaction with ferric chloride (blue in alcohol, violet in water) is only exhibited when two OH groups occupy adjacent positions, usually 3' and 4', on the nucleus. A typical example of the application of this knowledge to a structural problem is concerned with the anthocyanin of the peony. This substance, called peonin, is readily decomposed by boiling 20 per cent. hydrochloric acid to glucose and peonidin chloride,  $C_{10}H_{13}O_6Cl$ . This is  $CH_3$ , more than cyanidin chloride, and it can easily be shown that peonidin chloride is cyanidin chloride in which OH is replaced by  $OCH_3$ . Cyanidin iodide and  $CH_3I$  are obtained from peonidin by the action of hydriodic acid. Synthetical compounds of this series containing  $CH_3$  groups are numerous, and we know that, whilst  $OCH_3$  is about as powerful as OH in connection with the effect on the colour of the salt in acid solution, its influence on the ferric chloride reaction and the colour in alkaline solution is negligible.

Now, peonidin salts do not exhibit an intense ferric chloride reaction. Therefore the  $OCH_3$  is at 3' or 4'. The alkali reaction is however as strong as that of pelargonidin, and therefore OH in 4' is indicated and the  $OCH_3$  is at 3'. This view of the structure of peonidin chloride has been confirmed by synthesis (Method III). The position occupied by sugar groups in the anthocyanins may be elucidated in a similar manner. There are, for example, two diglucosides of cyanidin—namely, cyanin and mecocyanin (from the poppy). Both give intense ferric chloride reactions, and therefore have OH groups at 3' and 4'. The sugar groups must be attached to 3, 5 or 7, and if we blocked up any two of these with  $C_6$  sugar groups there would be no explanation of the strong alkali colour reactions of cyanin and mecocyanin. One OH must suffice to hold both molecules of sugar in each case, and we must be dealing with  $-OC_{12}$  rather than with two  $-OC_6$  groups. Cyanin gives a pure blue with sodium carbonate, but mecocyanin yields in this way a violet which changes to blue on the addition of sodium hydroxide. The synthetical flavylum salt with four OH groups in 3, 7, 3' and 4' has the colour reactions of cyanin, whilst that having OH groups in 5, 7, 3' and 4' has reactions almost identical with those of mecocyanin. It is, therefore, very probable that the  $-OC_{12}$  group in mecocyanin is in position 3 or 7, whilst in cyanin it is in position 5 or 7. For other reasons there is little doubt that the  $-OC_{12}$  group in mecocyanin is in position 3. Artificial anthocyanins—that is, flavylum salts with attached glucose molecules similar, but not yet identical, with the natural anthocyanins—have now been prepared in the Manchester laboratories (Method III). The restrictions which nature has laid on herself in the matter of anthocyanidins seem curious in comparison with the lavish production of variations in the structure of the closely related flavones and flavonols. The flavylum salts corresponding to all the naturally occurring flavones and flavonols must be regarded as potential natural anthocyanidins, and they have



almost all been synthesised. An indication that a derivative of one of these exists in nature has been obtained from a most unexpected quarter—namely, the rare red pigments prepared by Indians of Central America. Apparently, in preparing the colour, the leaves of *Bignonia chica*, a bushrope, are boiled with water, and particles of the bark known as “aryane” are added to the decanted liquid, causing the precipitation of the colouring matter. In 1914 Professor A. G. Perkin examined a specimen of “carajura” obtained from Manaos on the Orinoco, and isolated a crystalline red compound which he called carajurin. This has basic properties, and is decomposed by hydriodic acid, with formation of  $\text{CH}_3\text{I}$  (2 molecules) and carajuretin iodide. Subsequent investigations have shown that this salt has the same composition as pelargonidin iodide, and that it differs from the latter only in having an OH group in position 6 instead of in position 3. Carajuretin is, in fact, a fourth anthocyanidin, and is related in constitution to the flavone scutellarein. Naturally we are in the dark as to its mode of occurrence in the plant, but the method of preparation, which has been reported, is strongly suggestive of the hydrolysis of a glucoside by means of an enzyme. Few anthocyanins more urgently call for further investigation than that of the funnel-shaped violet flowers of *Bignonia chica*.

[R. R.]

Friday, April 23, 1926.

SIR EDWARD POLLOCK, F.R.C.S., Manager and Vice-President,  
in the Chair

RICHARD WHIDDINGTON, M.A. D.Sc. F.R.S., Cavendish Professor  
of Physics, University of Leeds.

### The Luminous Discharge through Rare Gases.

#### [SUMMARY.]

WHEN a current from a storage battery is passed through a vacuum tube containing Argon or Neon at low pressures, the discharge presents the usual ordinary appearance of positive column to the eye.

When viewed in a rotating mirror, the luminosity is seen to be regularly intermittent, consisting of brilliant coloured flashes moving quickly down the tube from anode to cathode.

The speed of these flashes is inversely proportional to the pressure of the gas, is determined to some extent by the value of the current, but is not much affected by the applied potential.

When the gas is impure the flashes are non-uniform, sometimes evidenced by a general wavy appearance in the mirror, sometimes by two clearly differentiated sets of flashes of differing speeds in two parts of the tube.

Possible theories of this new type of discharge are mentioned, and its relation to the well-known discharge phenomena discussed.

The form and character of the luminous discharge in the ordinary gases under conditions of low pressure and constant potential are quite well known. It will, therefore, be sufficient to pass these facts rapidly in review as an introductory to the new phenomena in the case of the rare gases.

A long glass tube evacuated to a pressure of 1 mm. of mercury or thereabouts, and furnished with plane electrodes, will, when fed with current from a constant potential of a hundred or so volts, present a characteristic appearance: the most important visible parts, proceeding along the tube away from the cathode, being the cathode dark space in which the luminosity is relatively faint, the

negative glow, the Faraday dark space, and then, filling the majority of the tube if it be a long one, the positive column.

The cathode phenomena in this ordinary type of discharge are perhaps the most arresting, and it may not be out of place for our present purpose to notice in passing the explanations and to perform one or two experiments.

The cathode is, of course, the seat of the cathode rays which stream away down the tube, ionising in their course. They are produced at or near the surface of the cathode by the impact of positive ions which originate most plentifully at and beyond the luminous boundary of the dark space. This space is dark because of the very high electric force obtaining there due to the space charge action of these positive ions, which high force prevents the re-combination essential to luminous emission. The dark space edge, therefore, marks the point at which the electric force has fallen to so low a value that the positive ions and the electrons from which they have been forced to part company are not so very rapidly swept past each other. It is a region of high conductivity. That this is the region from which the positive ions bombarding the cathode to produce electrons are drawn may be shown by this experiment.

A specially designed tube is furnished with a movable anode, which, when moved towards the cathode, produces no effect beyond the gradual disappearance of the part of the discharge through which it advances. The millimeter shows that the strength of the current is approximately maintained until the anode reaches the edge of the dark space. The current then suddenly stops. If the anode be moved back now, ever so slightly, the current begins to flow once more and luminosity reappears.

In passing, too, an interesting matter may be noted. If the anode is screwed back just to the point at which the discharge may be expected to recommence, but no further, a considerable delay may take place before it appears. If, however, a sample of radium be brought up, the current at once commences to flow, and we see the very thin layer of negative glow proper to the conditions of the tube.

The explanation in all probability is that a stray ion or so is necessary to the initiation of the discharge, and we are perhaps dependent on the natural ionization produced, maybe by the hard, all-pervading cosmic rays.

With the tube in the condition we chose, there is only a very thin layer of gas containing a comparatively small number of molecules available to this ionizing agency. The chance of ionisation is small; we must wait for it. If impatient we can increase the chance enormously by bringing up the stronger ionizing agent. The same result, of course, could have been effected by withdrawing the anode a little further.

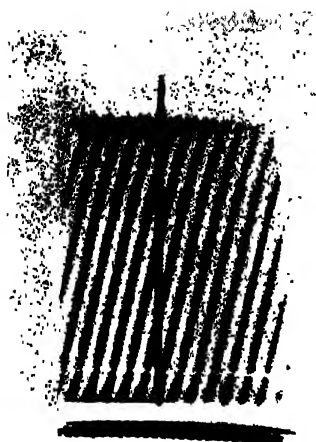


FIG. 2.



FIG. 3.



FIG. 1.

The important point, however, is that at a given gas pressure the anode and cathode must be more than a certain distance apart or the discharge goes out.

Reverting now to the tube in which the electrodes are a considerable distance apart, it should be pointed out that whereas very close to the cathode the field is determined in large measure by the potential applied, yet as points further and further away are considered the space charges become more and more important, until, when the positive column itself is reached, these space charges take control of the field almost entirely. Closely connected too with this matter of the space charge is the wall charge. This arises because both electrons and positive ions diffuse, the former more readily than the latter, with the result that the walls become negatively charged. There is thus set up a radial component of current which is of some importance in quantitative considerations.

The presence of this wall charge is rather well shown by an experiment in which the cathode is surrounded by a movable glass sheath. When this sheath is moved out over the cathode the pencil of cathode rays, originally broad, is compressed to a far narrower pencil as a result of the action of this negative wall charge.

It is a matter of some interest to notice here that experimenters with the luminous discharge have often found difficulty in maintaining the current perfectly steady. There is always a tendency for intermittency to appear, a regular oscillation often of very high frequency causing a note or hiss, for example, to be apparent in a telephone receiver included in the circuit. Yet in the striated form of discharge at any rate, viewing the tube in a rotating mirror reveals usually no discontinuities.

When a discharge tube containing a rare gas—argon for example—comes to be examined, new features are at once apparent. When the continuous positive column is viewed in a rotating mirror very obvious variations in luminosity appear.

When no special pains are taken to ensure purity of the gas, the appearance is very irregular (Fig. 1), but with argon carefully purified from hydrogen and nitrogen by the usual means, a very beautiful and regular appearance is presented (Fig. 2).

This can only be due to a perfectly regular sequence of luminous flashes travelling with approximately uniform speed down the tube from anode to cathode. Viewed directly, the so-called uniform positive column only is seen; viewed in the mirror its lack of uniformity is immediately obvious.

The inclination of the flashes is a measure of their speed, and by taking instantaneous photographs of the tube in the mirror simultaneously with a small mercury vapour arc fed with alternating current of power high frequency to act as a time-marker, the actual velocity of the flashes can be calculated. The speed varies with the pressure from about  $10^3$  to  $10^6$  cms. per second, and hardly depends

at all on the potential applied to the tube except in so far as this changes the current.

Very approximately the product of the speed and the pressure is constant, at any rate over ranges not too large.

The way in which the speed falls off with pressure is strikingly illustrated in Figs. 2, 3 and 4, the steeper (slower) flashes corresponding to the greater pressures.

It will be noticed, too, that the spacing between the flashes along the tube is roughly independent of the pressure over the range here considered. In other words, the tube contains on the average as many flashes at any instant at all pressures. Moreover, so far as the eye can judge, the flashes appear to be equally spaced.

When the tube has been running for a short time hydrogen appears in the tube, and in addition to the steep flashes a new, narrower and more horizontal set appears nearer the cathode, as in Fig. 5.

The spectrum reveals argon lines all along the tube, with the addition of hydrogen lines—strong near the anode—and are weak or absent near the anode.

It is natural to suggest that these flashes (or moving striations) consist of positive ions moving away from the anode; but it is by no means certain that this is the true explanation, and it will be used merely in a tentative manner, while an alternative, and possibly more likely, hypothesis will be introduced at a later stage.

An important point to notice is that so far as experiments with argon up to the present go, the spectrum of the discharge shows no vestige of the Döpler effect when viewed along the tube,\* whereas the resolving power of the spectroscope was certainly high enough to show the effect had it been present; it is to be supposed then that the motion of the flashes is apparent only, and may be regarded as a state of affairs consequent on the passage of "non-luminous" positive ions through the argon.

Although it has not been found possible to find a quantitative theory of this type of discharge owing to its very complicated and varying forms, it may be worth while here to suggest the manner in which these flashes may be generated and propagated on the view just mentioned.

The space near the anode will contain electrons which at the moment of applying the potential will commence to move up to the anode. Only those electrons originating from a plane further than a certain distance away from the anode will acquire ionising speed at the anode surface. When this sheet of positive ions is formed it

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\* The experiments at the time were thought to be fairly conclusive, but it has since been realised that flashes thought to have been due to argon may have been really hydrogen, which furnishes spectral lines unsuitable for observation at the temperature of working of the tube. The argument now put forward must therefore be regarded as tentative

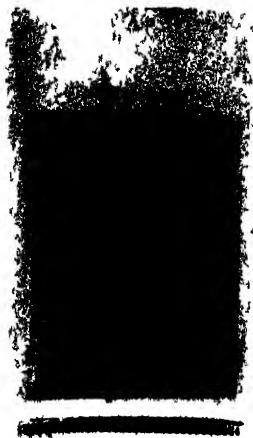


FIG 5



FIG 6



FIG 4

commences to move away from the anode as a space charge, which neutralises the field just behind it. The sheet is, therefore, quite thin, and moves away down the tube, its motion being marked by a patch of light apparently moving with it. The sheet may be regarded as acting as a virtual anode, attracting electrons to itself and so keeping up the supply of positive ions.

When it has moved a sufficient distance away a fresh sheet of positive ions is generated in the same way, which again moves off in its turn from the anode; thus a regular sequence of flashes is set up. At some distance away from the anode the motion of a flash is to be regarded as kept up by the repulsion of its successor.

If this be so it might be expected that the potential applied to the electrodes should not affect very much the speed of the flashes. That this is roughly true may be demonstrated by using a tube (containing neon in this case) of the kind used so extensively to-day for advertisement purposes. If an alternating potential of about 800 volts and 50  $\sim$  be applied, the characteristic and apparently uniform positive column is seen. On rotating a mirror slowly the field in the mirror is seen to be cut up by parallel dark lines corresponding to the zero points in the alternating potential. On rotating the mirror more quickly the bright field is seen to be crossed by rather wavy lines clearly of the type we have seen in argon, which reverse their slope at every half cycle. By suitably choosing the speed of our mirror we can select one half of the cycle only, so that attention is concentrated on flashes moving in only one direction down the tube. It is clear when this experiment is performed that, apart from irregularities due to impurities in the neon, the inclination of the lines seen in the mirror are about the same; they are all parallel and straight—that is, their speed in the body of the tube are all the same and independent of the applied potential. Near the electrodes, of course, this is not the case.

The speed of the flashes for any one gas appears to depend mainly on two factors—the current and the pressure. Over a limited range of gas pressure it has been found that the product of the pressure and the velocity is approximately constant. This means, of course, as our view of the phenomena would suggest, that at greater gas pressures the flashes move more slowly.

An interesting point is that over a very wide range of pressure, and therefore velocity, the flash spacing remains approximately the same; there are at any instant always about the same number of flashes present in the tube (usually three or four only with the tubes ordinarily used).

If the same charge is associated with every flash, this is what would be expected on our present view if below ionising speed the electrons suffer perfectly elastic impacts. The explanation—qualitative as it is—cannot really be so simple as this, for reasons which will be obvious from what follows.



Multiple excitation easily occurs in the rare gases, and evidence of this effect is not wanting in these discharges. The flashes often double, still retaining the same velocity, while an extreme case is shown in Fig. 6, where four distinct sets are shown in place of one.

If it were certain that the current in the tube was carried entirely by the flashes, it would be possible to calculate the charge associated with each flash, and thus the potential in the body of the tube under which the exciting and ionising electrons move. Attempts in this direction give the result that the potential fall involved is about 6 volts. The blue spectrum of argon is present, for which the lowest voltage of excitation so far recorded for high current densities is 19 volts. As the currents used in the present experiments run up to more than an ampere, it is possible that multiple excitation may account for this very low value. The calculation, however, rests on very doubtful assumptions, and no emphasis can be laid upon it. A very serious difficulty is that while the majority of the luminosity from the tube originates in the flashes, there is a distinct luminous background - whether emitting the same spectrum or not cannot so far be said: this is almost certainly associated with conductivity, and goes to vitiate any argument of the kind suggested.

When the flashes are followed up to the hot cathode, it is observed that their speed rapidly drops. This is doubtless due to the high conductivity of the gas in this region acting to reduce the electric force there.

The question of these moving flashes is by no means cleared up yet, for there are two very serious experimental objections to the hypothesis just outlined.

The first is, that if there is a considerable convection of gas in the form of ions along the tube, it should certainly be possible to detect a pressure distribution. This has not so far been observed.

The second is, that in the majority of cases so far examined oscillograph determinations of the current show no intermittency, or very little.

These objections would be removed, and most of the phenomena described would be explicable, if it be supposed that the flashes are due to atomic excitation and not ionisation.

The explanation would be somewhat as follows:—Electrons initiated in the cathode region and accelerated along the tube would attain energy sufficient for excitation at some definite plane, producing there a sheet of luminosity.

Just on the anode side of this plane there would thus be brought into existence a sheet of electrons at rest, constituting a space charge. Electrons would move away from this region and accelerate until they in their turn produced further along the tube a second sheet of luminosity, and so the process would be repeated.

On this view there is so far no reason to see why the luminosity should move towards the cathode. There must clearly be some

process at work which prepares in advance the atoms on the cathode side of the flash for impending excitation. This may be accomplished by actual diffusion of the excited atoms themselves, by radiation from them, or in some manner combining the two; but since no definite conclusion is possible at present, this bare mention of the speculation may suffice.

We come, in conclusion, to a rather interesting consideration which arises from the possibility of more than one set of flashes of different speeds existing at the same time in the tube. This might occur in the case of a mixture of gases.

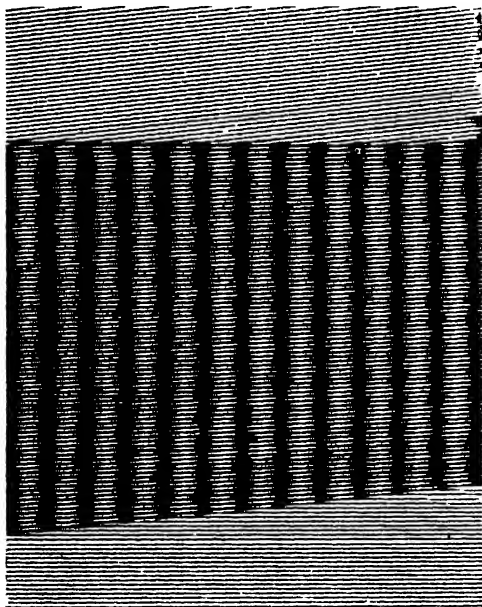


FIG. 7.

An impression of what the combined effect of two sets of flashes of unequal speed would be in the rotating mirror is given in Fig. 7, which is the result of superposing two coarse-ruled transparent gratings. This "moiré" effect gives straight, parallel bands, whose direction is that of the shorter diagonal of the parallelograms formed by the lines of the gratings. The inclination of these combination bands may be varied by turning one of the gratings.

It may be that this effect can be made a basis for the explanation of the stationary striations seen in mixtures of gases carrying currents at low pressures.

[R. W.]

Friday, January 21, 1927.

SIR ARTHUR KEITH, M.D., LL.D., F.R.S., Treasurer and  
Vice-President, in the Chair.

SIR WILLIAM BRAGG, K.B.E. D.Sc. F.R.S., Fullarian  
Professor of Chemistry.

### Tyndall's Experiments on Magne-Crystallic Action.

IN 1845 Faraday made the surprising discovery that the vast majority of substances, not merely iron, nickel and cobalt, were affected by a magnet, and showed also that the action was repulsive quite as often as attractive.

Faraday's results excited the greatest interest, and were the starting point for many other researches. In fact, they paved the way for the work of Thomson and Maxwell, who came thereby to the establishment of the laws of electro-magnetism. Among the many workers who followed Faraday was Tyndall, who made certain interesting discoveries relating to the behaviour of crystals in the magnetic field.

A very lively discussion sprang up as to the mode of interpretation of the new discoveries, particularly that of the so-called "diamagnetism." On the one hand, Faraday was satisfied that he could describe them in terms of his "lines of force": the majority, including Tyndall, referred everything to the existence of poles, magnetic and diamagnetic. Tyndall's experimental work, and the consequences which he drew from it, were devoted to the support of these views. When Faraday's conceptions prevailed it became clear that Tyndall's interpretation, of his own experiments in particular, must have been incorrect. His collected account of his researches published in the well-known "Diamagnetism and Magne-crystallic Action" never became a link in the chain of argument.

The recent analysis of crystal structure by means of X-rays throws some new light on those experiments of seventy years ago. We can see more clearly where Tyndall's conclusions were in error. But at the same time—and this has seemed to be of such interest that you might like to hear of it in the evening's discourse—the experiments of Tyndall are seen to be closely related to a modern

research of immense importance, that of the effect of stress on the constitution and physical properties of materials. Let me tell you the story.

On the 13th of September, 1845, Faraday made one of his most important discoveries, that of a relation between magnetism and light. He found that when plane polarised light was made to traverse a piece of his "heavy glass," a borosilicate of lead, in a direction coinciding with that of lines of magnetic force, the plane of polarisation was rotated. He had thus been successful in showing that the action of a magnet did not require the co-operation of a magnetic substance such as iron for its manifestation, but might be directly connected with a substance of a different kind, namely glass, and a different activity, namely light. In the following months he tried to find some other connection between magnetism and this glass. He floated his glass on a liquid and tried whether he could move it by a magnet, without result. But on November 4 he succeeded in his search. "The bar of heavy glass  $1\frac{1}{2}$  of an inch long and \* of an inch square was suspended by cocoon silk in a glass jar in principle as before and placed between the poles of the last magnet. When it was arranged and had come to rest I found I *could* affect it by the magnetic forces and give it position. Thus touching diamagnetics by magnetic curves and observing a property quite independent of light by which we may probably trace these forces into opaque and other bodies as the metals," &c. "If 1 was the natural position on making the poles magnetic the glass swung into position 2 and on to position 3. If contact was united after 2 the tendency to 3 was diminished, i.e. was less than if there ~~was~~ no current. If whilst swinging contact of current was continued during vibration from 1 to 2 and broken from 2 to 3, then united from 3 to 2 and broken from 2 to 1 the bar was soon sent spinning round the whole circuit" (Fig. 1).

The word "diamagnetic" is here used to denote substances through which, on his views, magnetic lines were passing. It is not yet used as an antithesis to paramagnetic. His new result obviously gave him intense pleasure, and in following it up he was so pre-occupied that he did not even go to the meeting of the Royal Society on November 20, when his paper on the "Action of Magnets on Light" was read.

We can easily repeat the experiment, using a piece of the same glass, taken from the store left by Faraday. It is not the actual piece, No. 174, as he tells us in his notes, for this cannot be found. The glass turns slowly in the magnetic field, and its motions are obviously controlled by switching the current off and on. The glass tends to set itself *across* the lines of force running from pole to pole, not *along* the lines as a piece of iron would do. And obviously the

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\* Not filled in, but from other notes we know it was half-an-inch square.

effect is very small as compared with the violent movements of iron under the same circumstances.

1823 If 1 was the induced position in making the poles magnetic the glass moving in the position 2 of or 1. position 3 If 1. position was induced after 2 the battery 1, 3 was connected & was left there if there was no current. If induced moving end 1. end was connected during induction from 1. 1 ? of battery from 2. 3. then moved from 3 to 2 of battery from 2. 1. 1 the bar came across




FIG. 1.—The above figure and a few lines of explanation are photographed from Faraday's original notes.

The action may be described as a repulsion of the glass by the magnet; and sometimes the early workers on the subject constructed apparatus specially designed to show the repulsive effect more obviously, and to distinguish it from a mere turning action in a magnetic field, if indeed this could be done. We can illustrate this point, and at the same time the diamagnetism of bismuth, by using a piece of apparatus constructed for Tyndall (Fig. 2).

Faraday at first suggested that the diamagnetic effect was the antithesis of the ordinary magnetic effect. A piece of iron when placed between two poles became so magnetised that a south pole was developed upon it in that part which was nearest to the north pole of the inducing magnet, and vice versa. Faraday's suggestion that the diamagnetic substance developed north and south poles where a magnetic substance would have developed south and north respectively was taken to be a satisfactory explanation. It was the constant endeavour of later experimenters to express their results in accordance with Faraday's hypothesis: even when development had reached a stage some distance ahead of that described in the original (Phil. Trans., 1846, p. 21).

Faraday was himself the first to feel doubts as to the satisfactory nature of his explanation. His early results could conveniently be described as showing an exact antithesis between two classes—where one was attracted by a magnet, the other was repelled; where one set itself in a certain direction in the magnetic field, the other avoided that direction as much as possible. It seemed proper to describe them as being in exact antithesis to each other, and the word diamagnetism was adopted as a means of expressing the experimental result.

He prepared a list of substances which showed varying degrees of

response to the action of the magnetic field, and the plan of the statement illustrates his first views (Exp. Res., Vol. III., Series XXI., 2424):

Iron	Alcohol
Nickel	Gold
Cobalt	Water
Manganese	Mercury
Palladium	Flint glass
Crown glass	Tin
Platinum	Heavy glass
Osmium	Antimony
0° Air and vacuum	Phosphorus
Arsenic	Bismuth
Ether	

It is to be observed that those preceding air and vacuum are to be considered above zero or magnetic, those succeeding,

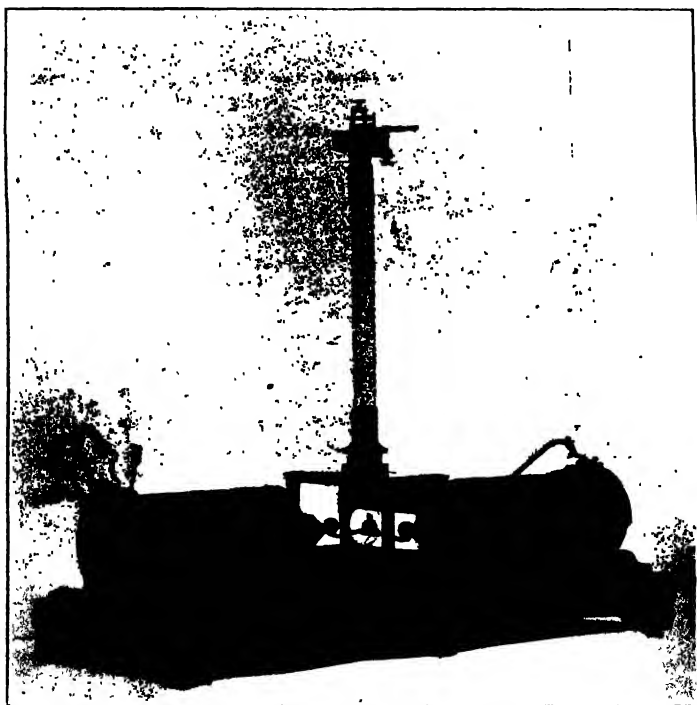


FIG. 2.—Apparatus used by Tyndall. Two balls of bismuth are placed at opposite ends of an arm swinging at the end of a suspension thread. The electro-magnets are staggered so as to combine their actions in turning the arm by means of the repulsive forces exerted on the balls. ("Diamagnetism and Magnetic-crystalline Action," p. 53.)

below zero or diamagnetic, which is meant to imply a true antithesis.

In December, 1845 (Exp. Res., Vol. III., Series XXI., 2429), Faraday writes:—

“Theoretically, an explanation of the movements of the diamagnetic bodies, and all the dynamic phenomena consequent upon the actions of magnets on them, might be offered in the supposition that magnetic induction caused in them a contrary state to that which it produced in magnetic matter—i.e. that if a particle of each kind of matter were placed in the magnetic field both would become magnetic, and each would have its axis parallel to the resultant of magnetic force passing through it; but the particle of magnetic matter would have its north and south poles opposite, or facing towards the contrary poles of the inducing magnet, whereas with the diamagnetic particles the reverse would be the case; and hence would result approximation in the one substance recession in the other.”

But even at that time his views were not firmly established; and we may repeat an experiment of his which shows the nature of the contrary influences that were impressing him. A small glass tube filled with a weak solution of the magnetic substance, iron sulphate, sets itself axially between the magnetic poles. But if it is surrounded as it swings by a strong solution of the same substance it sets equatorially. The tube appears to be magnetic as compared to air, but diamagnetic as compared to the strong solution.

Might not, on this analogy, all substances and also air and vacuum be magnetic, reacting to the magnet in the same way, but to different degrees? And might not bismuth exhibit its peculiarities, not because it was in antithesis to iron, but merely because it was less magnetic than the air? Yet he writes as follows: “Such a view also would make mere space magnetic and precisely to the same degree as air and gases. Now though it may very well be that space, air and gases have the same general relation to magnetic force it seems to me a great additional assumption to suppose that they are all absolutely magnetic, and in the midst of a series of bodies, rather than to suppose that they are in a normal or zero state. For the present, therefore, I incline to the former view and consequently to the opinion that diamagnetics have a specific action antithetically distinct from ordinary magnetic action, and have thus presented us with a magnetic property new to our knowledge” (Exp. Res., Vol. III., Series XXI., 2440, Dec. 1845). The extract describes his first-formed opinion.

The next important step is due to Plücker:—

“In 1847 Plücker had a magnet constructed of the same size and power as that described by Faraday, his object being to investigate the influence of the fibrous constitution of plants upon their magnetic deportment; while conducting these experiments, he was induced to try whether crystalline structure exercised an

influence." \* The first experiment made by Plücker gave an immediate and decided reply. The investigation of the behaviour of several crystals led him to announce the following laws :—

"When any crystal whatever with an optic axis is brought between the poles of a magnet, the axis is repelled by each of the poles ; and if the crystal possesses two axes, each of these is repelled with the same force by the two poles.

"The force which causes this repulsion is independent of the magnetism or diamagnetism of the mass of the crystal ; it decreases with the distance more slowly than the magnetic influence exerted by the poles."

There is some truth in Plücker's conclusions, but much correction is necessary. Tyndall pointed out in 1850 that they broke down completely when applied to calcium and iron carbonate. These two crystals are isomorphous ; the former, Iceland spar, obeys Plücker's laws in that it sets its axis equatorially in the magnetic field, but iron carbonate sets its axis from pole to pole. Plücker had, however, done great service in calling attention to the peculiar behaviour of crystals in the magnetic field.

In the autumn of 1848 Plücker was in London. Faraday writes in his laboratory notes :—

"16 Aug. 1848. Plücker has described to me certain of his results as to the crystalline diamagnetic relation and, as I understand it, the optic axis of a crystal having *one* optic axis tends to pass into the equatorial direction, or if a crystal have two optic axes then the line between them tends to pass into the equatorial direction."

"25 Aug. 1848. To-day Plücker showed me for the first time some of his experiments.

### *"First Optical Results.*

"A small rhomboid of Cal<sup>c</sup> Spar was suspended by a single cocoon thread between my Elect. Magnet poles with the optic axis in a horizontal position. When the poles were very close as in the figure the diamagnetic force of the substance made it take the position shown in which the optic axis is axial to the magnet. But when the poles were opened out to distance of half or three-quarters of an inch, then the mass pointed axially and the optic axis therefore equatorially (Fig. 3). . . There is a given distance between the Mag  
or piece

poles (pretty close) when a certain rhomboid of Cal<sup>c</sup> spar between them is so affected that the diamagnetic and the magneto optic force is balanced at smaller distances the piece points diamagnetic and at larger distances Magneto optic. So that on increasing the distance the magneto optic force diminishes *less rapidly* than the

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\* Tyndall, "Diamagnetism and Magne-crystallic Action," p. 2.



magnetic force and on diminishing the distance it increases *less rapidly* than the magnetic force. *But increasing or diminishing the strength of the magnet produces no alteration of this place of neutral action, it only increases or diminishes the strength of the action on each side of it:—or rather the resultant of the two actions on each side of that neutral position.* So Plucker at least tells me for I did not see that proved."

Plucker's experiment is readily shown: but a little care in adjustment is required. The dimensions of an equal-sided rhomb are rather too much the same in all directions: a somewhat more irregular piece is I find easier to work with. The effect is much more clearly seen with a good bismuth crystal which has been

25 Aug 1848

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*25 Aug. Plucker showed me for the first time some of his experiments.*

*First Expt. result*

*A small shunt of Bismuth was suspended by a single wire thread between my North Magnet poles*

*with the plate axis in a horizontal position. When the poles were very close as in the figure the magnetic force of the solution*

*made it take the position shown in which the plate axis is equal to the magnetic. But when the poles were spread out to distance of half an inch or more it was much then this magnet pointed equally to the plate axis therefore symmetrically.*

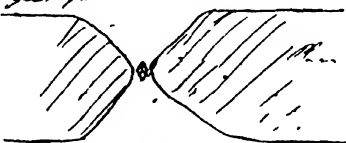


FIG. 3.—The figure is taken from Faraday's notes, August 25, 1848

obtained in the following way. A little bismuth was melted in a glass tube which had been drawn to a point. The tube was placed in an electric furnace, from which it was made by clockwork to emerge very slowly. The fine end of the tube came out first, and the bismuth at the point was the first to solidify into crystalline form. The rest of the metal crystallised slowly as the emergence proceeded, and under the circumstances continued the structure and orientation of the first fragment. In this way, due to Bridgeman, the mass contained large single crystals, not a mass of fine crystals as is usual when the solidification takes place rapidly.

When the crystal, which is ten times as long as it is broad, is placed in the magnetic field due to pointed poles, it sets strongly

equatorially in accordance with the usual behaviour of a diamagnetic body; but when the poles are withdrawn somewhat it sets axially with equal strength.

The experiments of Plücker introduced a new effect which Faraday subsequently called "Magne-crystallic Action." It clearly deserved a name, since its manifestations added a complication to the diamagnetism which had already been observed.

The new discoveries presented so many forms when repeated with different crystals suspended in different ways and with different forms of magnetic field that the complications were not unravelled for some years. Some of the difficulties were due to the circumstances of the experiments, and had no relation to the real question. One of these incidental effects was that of attractions and repulsions due to transient currents induced in bodies already suspended for observation between the magnetic poles when the magnets were excited. As is well known the motion of a spinning block of copper is at once arrested by the action of such currents; on the other hand, a sheet of copper held near a pole is sharply repelled when the current is turned off, and if properly suspended can be set into a rapid spinning. These effects had nothing to do with diamagnetism, but they were apparently the cause of confusion on some occasions.

Another great source of difficulty was the overpowering effect of iron impurities; the diamagnetic effects are so feeble in all cases that a mere trace of iron, nickel or cobalt is sufficient to mask them. So, for instance, Plücker's experiments with antimony seem on this account to have been at variance with the true facts as proved by Faraday.

In 1848 Faraday published a series of researches on the magne-crystallic phenomena, which cleared up some of the difficulties. But in 1850 he could still write as follows:—

"Four years ago I suggested that all the phenomena presented by diamagnetic bodies, when subjected to the forces in the magnetic field, might be accounted for by assuming that they then possessed a polarity, the same in kind as, but the reverse in direction of, that acquired by iron, nickel and ordinary magnetic bodies under the same circumstances. This view was received so favourably by Plücker, Reich and others, and above all by W. Weber, that I had great hopes that it would be confirmed; and though certain experiments of my own did not increase that hope, still my desire and expectation were in that direction. (2641.) Whether bismuth, copper, phosphorus, etc., when in the magnetic field are polar or not, is however an exceedingly important question; and very essential and great differences in the mode of action of these bodies under the one view or the other, must be conceived to exist. I found that in every endeavour to proceed by induction of experiment from that which is

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\* Tyndall, "Diamagnetism and Magne-Crystallic Action," p. 16.

known in this department of science to the unknown so much uncertainty, hesitation and discomfort arose from the unsettled state of my mind on this point that I determined if possible to arrive at some experimental proof either one way or the other. This was the more important because of the conclusion in the affirmative which Weber had come to in his very philosophical paper. . . (2642.) It appeared to me that many of the results which had been supposed to indicate a polar condition were only consequences of the law that diamagnetic bodies tend to go from stronger to weaker places of action; others again appeared to have their origin in induced currents. . ."

Accordingly he undertook a further series of researches which in the end brought him to regard all his effects as expressible in the simple form with which we are familiar. In his "Experimental Researches" (Vol III., Ser. XXVI., Oct. 1850, 2807), he writes:—

"When a paramagnetic conductor, as for instance a sphere of oxygen, is introduced into such a magnetic field considered previously as free from matter, it will cause a concentration of the lines of force

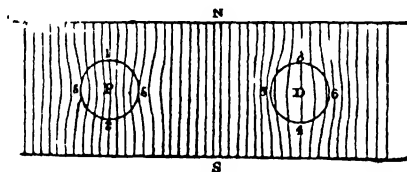


FIG. 4.—The figure is taken from Faraday's *Experimental Researches*, and was drawn to show his conception of the passage of lines of magnetic force through paramagnetic and diamagnetic bodies respectively.

on and through it so that the space occupied by it transmits more magnetic power than before. If, on the other hand, a sphere of diamagnetic matter be placed in a similar field it will cause a divergence or opening out of the lines in the equatorial direction and less magnetic power will be transmitted through the space it occupies than if it were away" (Fig. 4).

This describes diamagnetism generally; the complication of magne-crystallic action is described with equal simplicity:—

"(2837). If the idea of conduction be applied to these magne-crystallic bodies, it would seem to satisfy all that requires explanation in their special results. A magne-crystallic substance would then be one which in the crystallised state could conduct onwards, or permit the exertion of the magnetic force with more facility in one direction than another; and that direction would be the magne-crystallic axis. Hence, when in the magnetic field, the magne-crystallic axis would be urged into a position coincident with the magnetic axis by a force correspondent to that difference, just as if two bodies were taken,

when the one with the greater conducting power displaces that which is weaker."

It is only a uniaxial crystal of course which possesses a single magne-crystallic axis; it is the axis of a certain spheroid. The facility of conduction in different direction in a biaxial crystal requires an ellipsoid for its representation.

This way of stating the rules allows us to see at once the principle of the experiments which Plücker showed to Faraday, and which the latter so greatly extended. When the magnetic poles were close, the crystal occupied a part of the field where the lines of force were very divergent. Under such circumstances the orientation of the crystal would be determined by the general tendency for diamagnetic bodies to move from the stronger to the weaker parts of the field, and the crystal set its longer dimension perpendicular to the field; the optic axis was then parallel to the lines of force. But when the magnetic poles were separated the crystal covered a part of the field in which there was little divergence; the magne-crystallic action then took charge, and the crystal set itself so that the direction of worst conduction of the lines, i.e. the optic axis, was at right angles to the lines.

A few simple experiments will serve as further illustration of these rules. We take a crystal of sulphate of iron which has the form of a thin plate; the flat sides are cleavage planes and the "conducting power" for Faraday's lines is far greater across the plate than along the large faces. In a uniform field the crystal plate sets equatorially therefore, and even when allowed to move up to one of the poles keeps its face normal to the lines. A thin plate of iron would stand on edge on the pole; but the magne-crystallic action of this paramagnetic crystal is exceedingly strong.

A bismuth crystal so suspended that its axis (it is a uniaxial crystal) is vertical has no magne-crystallic action. Its motions are governed by the general tendency of its mass to move from the stronger to the weaker parts of the field; in a uniform field it has no appreciable tendency to set itself in any particular direction. But when the crystal is hung so that the axis is horizontal, that axis tends strongly to set itself along the lines of force, as we saw before.

Naphthalene is a monoclinic crystal. Its magne-crystallic properties are represented by an ellipsoid, one axis of which coincides with the single axis of symmetry. The cleavage is very perfect and the crystals take the form of thin plates parallel to the cleavage planes. The axis is also parallel to the cleavage planes and if the crystal is suspended so that this axis is horizontal and the cleavage planes vertical, the axis and the planes move into the equatorial position, thus fulfilling the requirements of symmetry. But when the crystal is hung, in a uniform field, so that the axis is vertical the cleavage planes set themselves at a certain angle to the field. One of the axes of the magnetic ellipsoid then lies along the lines, another across

them ; the third is vertical. There is no obvious relation between the cleavage plane and the first two axes. Finke\* has shown that this may be said of various crystals examined by him. If now the crystal be suspended from the other end of the axis, its cleavage planes will make the same angle with the field, but on the opposite side of the medial line (Fig. 5). Faraday describes results of this kind which he obtained with a paramagnetic crystal of sulphate of iron (Exp. Res., Vol. III., Series XXI., 2634-7). Naphthalene is

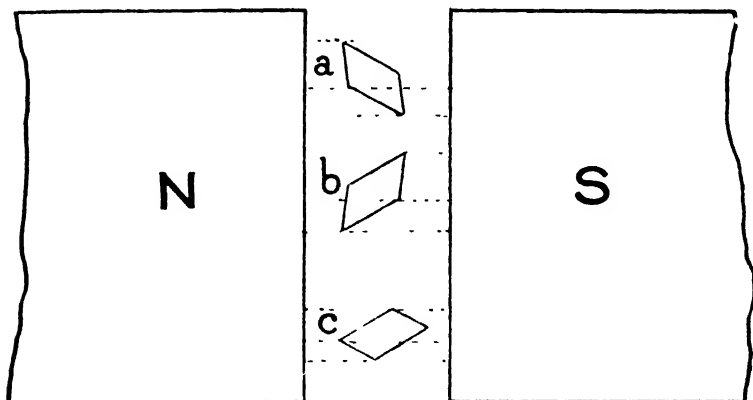


FIG. 5.—In this figure the positions marked *a* and *b* are positions of equilibrium of the naphthalene crystal in the magnetic field. The axis of symmetry is vertical and perpendicular to the plane of the paper. The cleavage plane is also vertical, and its intersection with the plane of the paper is the longer side of the rhomboid. The form of the crystal shown in the figure is not a natural form because the shorter side of the rhomboid is drawn parallel to one face of the cell of the crystal lattice, which face does not usually occur on the crystal. It is so drawn in order to show the relation between magnetic lines and the lattice.

If the crystal is hung from one end of the *b* axis the position *a* is assumed, and if from the other the position *b*. The position *c* is impossible.

diamagnetic ; like many other organic crystals it shows the magne-crystallic effect very strongly.

These experiments will serve to show the great variety of effects that may be observed. All of them are, however, easily correlated by Faraday's conception of lines of force. Let us remember that there are several variables and give due importance to each. The first of these we call diamagnetism, implying that the lines pass through the substance in question less easily than through the air or a vacuum. The second is called magne-crystallic action, in

reference to the fact that in a crystal the lines pass more easily in one direction than another. A third variable is the crystal shape, which may also affect the set in the magnetic field when the latter is divergent. A fourth is the amount of divergence of the field which, in a uniform field, falls to zero. All these influences have to be taken into account after experimental disturbances have been allowed for.

The more divergent the field the more does the simple diamagnetic effect assert itself, and any magne-crystallic action which would tend to make the specimen set a crystal axis or axes at some particular inclination to the direction of the field is overpowered.

On the other hand, magne-crystallic action usually takes charge in a truly uniform field. For the sake of brevity and an easier explanation it may be well to call attention to a fact which was not fully appreciated by all the first experimenters, but was clearly set out by Sir William Thomson (Lord Kelvin) in 1885. A diamagnetic bar, apart from magne-crystallic action, tends to set itself *along* the lines of force in a *uniform* field, just as a paramagnetic bar. Imagine the bar to be made up gradually of a collection of cubes, placed successively one after the other in the magnetic field. The effect of the presence of the first cube is, as we should say in the language of Faraday, to spread out the lines of force on their way through the cube, and to crowd them together on either side of it. A second diamagnetic cube will, if free to move, go to that part of the field where the lines are least crowded; it will therefore avoid setting itself beside the first cube and prefer to place itself in front or behind it. A third will continue the same process, and in the end the cubes will form a bar pointing along the lines. In the case of a substance such as iron, there is a double converse. The lines are most dense just in front and just behind the first cube; and a second cube will place itself in one of those positions because a magnetic substance seeks for the strongest part of the field. Again, therefore, the bar grows along the line as, in this case, we know from experience (Fig. 6).

It is certain that no one has ever seen the first of these effects because it must be so minute and difficult to separate from others. We may safely infer it, as Thomson pointed out, because our theories of the electromagnetic field have been abundantly justified by other means. The susceptibility of bismuth, by far the most diamagnetic substance, is only about  $10^{-6}$ ; in other words, the strength of the field on one side of a bismuth cube of 1 cm. side would only be about a thousandth part of one per cent. greater than at the front or back of the cube. Near a pointed pole the strength of the field might easily vary by fifty per cent. in a centimetre. It is easy to see how feeble is the force tending to arrange the supposed cubes parallel to the lines of a uniform field as compared with the forces acting on a bar placed near the pole.

The analogous effect in electrostatics can however be realised. When two plates are immersed in oil and maintained at a large difference of potential, an elongated rod of glass hung from a fibre, sets itself along the lines of force ; to make sure that the effect is true

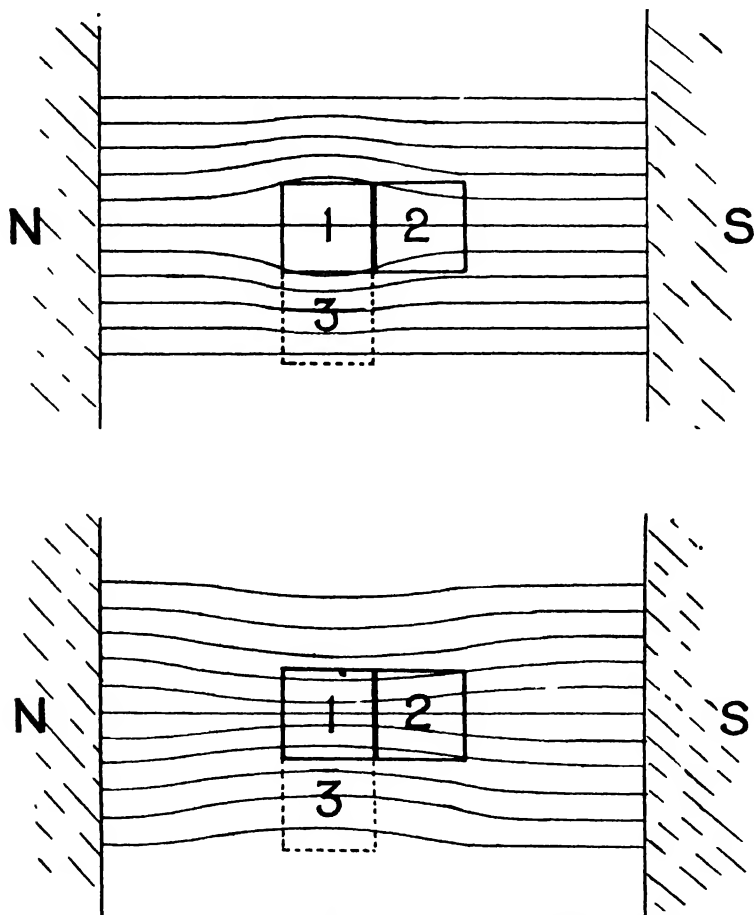


FIG. 6. -Dia- and paramagnetic substances in a magnetic field.  
In both cases Position 2 is preferred to Position 3.

the rod must be free from any conductivity due to its own substance or a water film. This corresponds to the setting of a magnetic body in a uniform field. When bubbles of air are allowed to rise through the oil they are drawn out along the lines of force,\* which

\* I am so informed by Capt. Dunsheath of the Henley Telegraph Works Co.

effect, since the inductivity of air is less than that of oil, represents the setting of a diamagnetic body along lines of magnetic force.

When a diamagnetic substance sets itself across the lines of a magnetic field, and no magne-crystallic action is at work, it is because the field is not really uniform. It is perhaps a little confusing when it is said, as is sometimes the case, that diamagnetic and paramagnetic substances are the antitheses of one another in that one kind sets itself across the field and the other along it. This is only true of a field which is non-uniform. Indeed, it may be said that the use of the word antithesis is incorrect in any case. There would be a true antithesis if one substance could be defined by its pointing along the lines of force in one direction while another pointed in exactly the opposite direction; there is no true antithesis between pointing along the lines and pointing across them. It seems to me, though I say it with diffidence, that this difficulty was stirring in Faraday's mind, and was the true cause of the uneasiness of which he spoke in a quotation given above, and of his aversion to the description of diamagnetism and paramagnetism as being the antitheses of one another.

Faraday, as I have said, when this thorough examination of the facts had led him to frame a hypothesis which would link them together, based his interpretation on the existence of lines of force, and found himself able to place both his own results and those of others in their place within a self-contained system.

Kelvin placed this hypothesis in mathematical form, thus completing the treatment of the subject of magnetism by Poisson; the latter had left out of his consideration the consequence of magnetic susceptibility being different in different directions, not because he overlooked the possibility of such an effect, but because no case of its occurrence was known to him.

But Faraday's views were not accepted by other experimenters on the same subject, and in particular by Tyndall. The idea of polarity was not to be given up easily, and innumerable experiments were made to show that a "diamagnet" had poles like a magnet, but in the opposite sense. A bar of bismuth would develop north and south poles, when under similar circumstances a bar of iron would develop south and north. And, of course, when the facts are prepared for mathematical treatment they can be expressed in this way. It is generally convenient and justifiable to represent a magnet by two poles because the form of the field at any reasonable distance is satisfactorily represented thereby, though in the immediate neighbourhood the lines of a real magnet do not run like those of the theoretical bipole. Within the body of the magnet the lines run from the south pole to the north, continuing and completing their course outside, so that every line is a closed circuit; but all lines near a bipole run from the north pole to the south pole. So also in the magnetic shell, which is in the mathematical treatment the exact



analogue of the electrical condenser, the bulk of the lines run from one plate to the other across the narrow space between the two plates; comparatively few run from the outside of one plate, through surrounding space, to the back of the other. In the condenser the internal field is the more important, the external being looked on as a correction. In the magnetic shell the reverse is the case; the outside field is that which is considered because it represents more and more closely, as the plates are brought closer together, the field due to a current circulating about the contour of the condenser. The theoretical charges on the plates have to be made larger and larger as the plates are brought together so that the strength of the outside field may remain the same.

Now, if a piece of bismuth is placed along the lines of a magnetic field, the lines avoid the piece to some extent, though, as already explained, the avoidance is extremely small. If we take the bismuth away and replace it by a feeble bipole consisting of south pole magnetism, of proper amount, where the lines come out of the bismuth and a corresponding amount of north pole magnetism where they go in, the whole arrangement being made in a vacuum, or, permissibly, in the air, we get in this artificial way an external field resembling that which exists when the bismuth is in place (Fig. 7). It can be said that polarity is developed in the bismuth in a sense opposite to that which is to be found in iron under the same circumstances. If the effect is to be represented, for the convenience of treatment, as due to the presence of a bipole, then the sense of the bipole in the case of bismuth is opposite to the sense in the case of iron. The old argument therefore was not between two hypotheses but two languages in terms of which the facts were to be described. Such an antagonism, once believed in and debated, could be, and was, the cause of an immense variety of experiments devised to justify one side or the other. But Faraday felt that his way of putting the facts was more fruitful in suggestion of further experiments, and more convenient as a foundation for theoretical development. He has been abundantly justified.

We now come to the part which Tyndall played in a debate which was conducted on both sides in such an able, and, it is pleasant to observe, in such a friendly way. In the first place, Tyndall and Knoblauch published in 1850 an account of experiments which they had made. They showed that Plücker's first views, those which included the repulsion of the optic axis of a uniaxial crystal by the poles of the magnet were, as already stated, incorrect in many cases, and they substituted an amended set of rules in the following terms:—

“ If the arrangement of the component molecules of any crystal be such as to present different degrees of proximity in different directions, then the line of closest proximity, other circumstances being equal, will be that chosen by the respective forces for the

exhibition of their energy. If the mass be magnetic this line will set axial, if diamagnetic equatorial."

The key-word is "proximity." This condensed statement, of course, requires explanation. Tyndall supplies it in full in his book on "Diamagnetism and Magne-crystallic Action." A brief summary will be sufficient for our present purpose. In the first place, the ob-

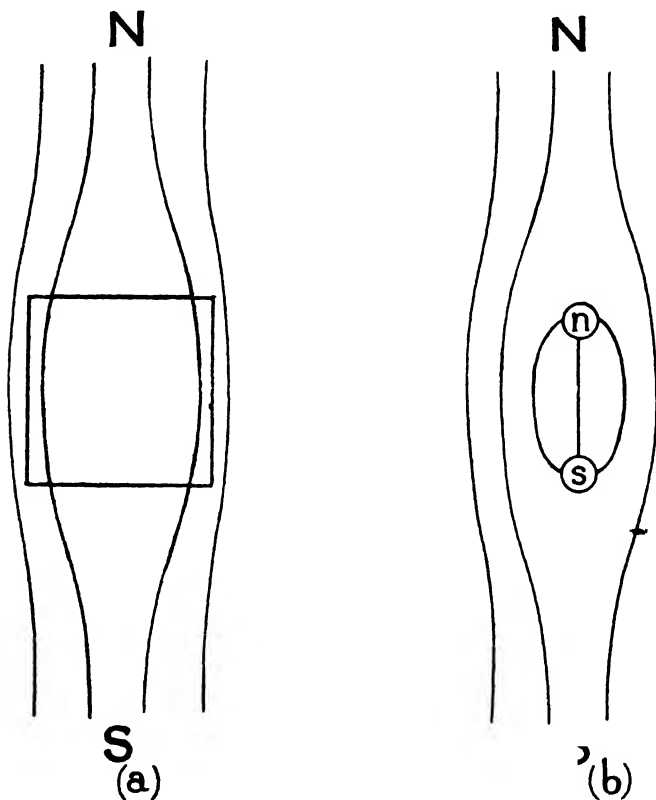


FIG. 7.—For explanation see the text.

servations made by himself and his partner on the behaviour of crystals in the magnetic field convinced them that the plane of cleavage determined in a number of cases the position which the suspended crystal would take. Magnesium sulphate, zinc sulphate, saltpetre, and topaz were diamagnetic substances, and their cleavage planes, the crystals being so suspended that these planes were vertical, always set themselves equatorially, i.e. at right angles to the field. On the other hand,

nickel sulphate, scapolite and beryl, which were magnetic crystals, under the same circumstances set their cleavage planes parallel to the field. The connection between these results and the statement quoted above lies in this, that the molecules in a crystal were supposed to be in greater proximity along a cleavage plane than in any other direction. Let us take bismuth as an example. It is diamagnetic and sets its cleavage plane equatorially in accordance with Tyndall's rule. Its structure has now been determined by X-ray analysis, so that we can see what meaning can be attached to the claim for proximity in the plane of cleavage. The bismuth structure can be looked on, approximately, as a slightly distorted cube; one of the cube's diagonals has been a little stretched, while the other three have been left unchanged. The crystal is then uniaxial; the axis is the stretched diagonal; the principal cleavage plane is perpendicular to the axis. The spacing of the planes parallel to the cleavage is larger than that of any other set of planes in the crystal, and these consequently contain more molecules to the unit area than any other planes. Tyndall would have said that in those planes there was a maximum proximity between the molecules.

The X-ray analysis of other crystals often shows the cleavage plane to have the largest spacing and therefore the closest degree of packing. This means that the points of the crystal lattice are closest together in that plane, but it does not mean that the atoms or molecules are nearer together in that plane than in any other. Nothing can be said about that until the actual distribution of the atoms in the unit cell has been determined. It would be much safer to say that the existence of a cleavage plane implies a certain *looseness of packing across* the crystal planes, which are parallel to the cleavage. This would imply a greater tightness in other directions, but not necessarily a greater proximity. It is only at first glance that the latter term seems to have a clear meaning. But we must let it stand in order to realise the argument as it presented itself to the authors of the statement quoted.

It happens that in the case of bismuth we do actually find a closer bonding between the atoms in the cleavage plane than in any other; but this is peculiar to the structure of bismuth, and has no relation to the supposed close proximity of *molecules* in the cleavage plane.

Now we come to the essential point of the argument. It is supposed that proximity offers magnetism or diamagnetism, whichever it may be, the opportunity to "exhibit its greatest energy." We are to remember that the hypothesis on which we are working expresses itself in terms of poles, and that a magnet attracts a piece of iron by inducing poles in it, which poles then react with the poles of the magnet. When a piece of iron is allowed to attach itself to a magnet, the poles induced in it are much stronger than if the

magnet and the iron are separated by a little distance. If a second piece of iron is brought near the first, every increase in its proximity increases the strength of the poles which are developed in this piece by the influence both of the original magnet and of the first piece

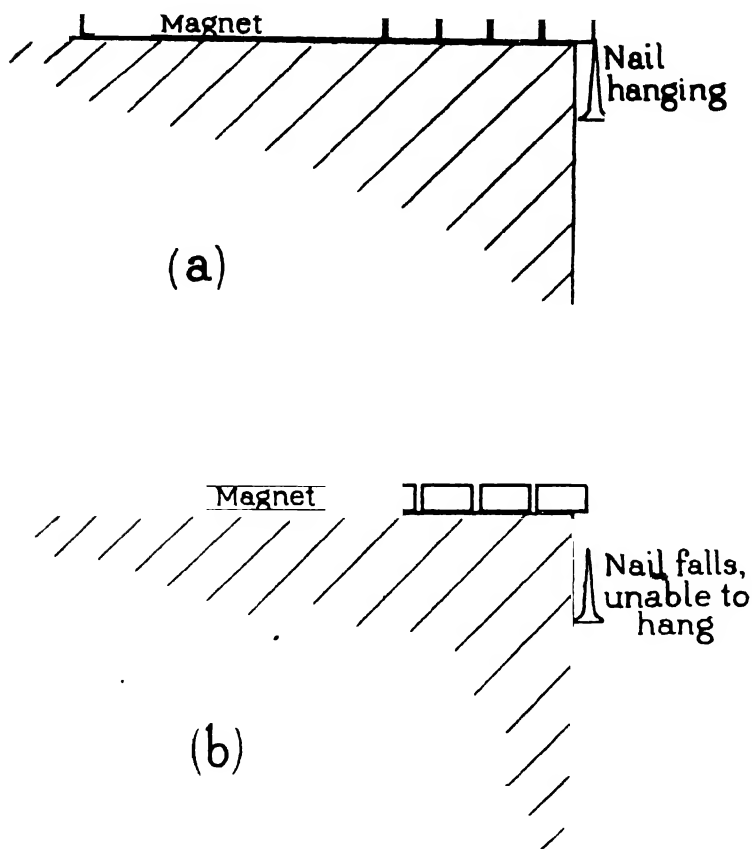


FIG. 8.—When pieces of iron are all in contact with one another and the end one with the magnet, the nail can hang as shown in (a). But when, as in (b), the iron blocks are somewhat separated from the magnet the nail falls.

of iron. A simple experiment will serve as an illustration (Fig. 8):—The nail hangs in the first case, and not in the second, because the close proximity of the iron blocks increases the strength of the poles in all of them. In the second case, the nail will not hang, although the

magnet is actually closer to it. The benefit of mutual "proximity" of the separate pieces of iron is obvious. An equally simple explanation can be given in terms of lines of force, but we are using the alternative language.

Chains of iron fragments form readily between magnetic poles of opposite nature. A rod of iron "transmits the magnetic force," and generally acts more efficiently than a set of iron fragments which are not allowed to get into close proximity with each other. Tyndall sticks short lengths of iron wire through disc-shaped pieces of apple, and shows that the disc set itself at right angles to the field, the bits of wire therefore lying parallel thereto. In each bit are many molecules of iron in close proximity, and the fact is more effective in directing the apple than the existence of a number of bits scattered over the disc without being in "proximity" to each other.

It is now argued by Tyndall that if the magnetic influence of a magnet is extended by means of proximity, the diamagnetic influence must be extended in the same way. If the close proximity of iron fragments will help them to set with greater firmness in the direction joining opposite poles, then the closer proximity of bismuth fragments should cause them to set with greater firmness across them. In this way Tyndall interpreted the rule, which he believed he had established, that the cleavage planes of magnetic crystals tended to set axially, and those of diamagnetic crystals equatorially.

It is interesting to observe that Tyndall was attempting to supply both a rule for the setting of crystals and an explanation of the rule in terms of structure. Faraday stopped short when he had supplied a picture of the distribution of his magnetic lines, or, as we should now say, a map of the distribution of energy in the magnetic field.

As I have already pointed out there is no clear meaning to the term "greater proximity in the cleavage plane." Moreover, if conclusions were to be drawn from analogy with phenomena on a larger scale they would run contrary to the intended argument; for on that scale at least a line of diamagnetic masses tends to set itself axially, not equatorially. Moreover, a piece of bismuth makes an extremely minute alteration in the disposition of the lines of force, for which reason it is a very poor detector of the existence of the lines in comparison with iron; and the change, since it is so small, can indeed be detected by a piece of iron in the form of a magnet, but certainly not by another piece of bismuth, no matter how close they are together.

In the case of a uniaxial crystal a principal cleavage must from symmetry considerations be related to the axis and, if it is unique, must be perpendicular thereto. When there is more than one cleavage, the cleavage planes must be symmetrically disposed about the axis, as in the case of Iceland spar. It is not therefore surprising that in the former case the cleavage plane should place itself exactly,

either equatorially or axially, and that in the latter case a plane perpendicular to the axis might be looked on as a resultant of cleavage planes and therefore set itself equatorially. But it does seem remarkable that, as Tyndall pointed out, the substitution of iron for calcium in Iceland spar, to form the isomorphous iron carbonate, should turn the structure round through  $90^\circ$  in the magnetic field; especially if we assign diamagnetism and paramagnetism to different causes. It may be there are other cases of the same change; and any rule of this kind must clearly be of importance.

We now come to another set of experiments, very interesting and important, which were used by Tyndall in the defence of the "polarity" position. The method of these experiments was suggested by an accident. When working in Berlin with a fine magnet placed at his disposal by Magnus he was observing the action of the magnet on a bismuth cube which was so shaped that two opposite faces were perpendicular to the optic axis and parallel to cleavage planes. When the current was switched on the magnetic poles rushed together because the separate parts of the magnet had not been properly bolted down. The bismuth cube was crushed to some extent. Working conditions having been restored, it was found that the bismuth set itself at right angles to its former position. The line of pressure, which of course had been parallel to the field, was now perpendicular to it. Tyndall now argued that the particles of bismuth had been brought into greater proximity by the pressure, and that the setting of this line of great proximity was in accordance with the rule given by himself and Knoblauch. So began an extended series of researches on the effects of pressure which are fully described in his book. As an example let us take the following:—

"A quantity of bismuth was ground to dust in an agate mortar, gum-water was added, and the mass was kneaded to a stiff paste. This was placed between two glasses and pressed together; from the mass when dried two cubes were taken, the line of compression being perpendicular to two of the faces of each cube and parallel to the other four. Suspended by a silk fibre in the magnetic field, upon closing the circuit the line of compression turned strongly into the equatorial position . . ."

When carbonate of iron was used the line of pressure set axially.

Such an experiment is very striking, whatever its explanation may be. Tyndall argued that he had by compression increased the proximity along the line of pressure, but it is difficult to see how this can be. If a number of particles of one kind are distributed with complete irregularity in a paste medium which is then subjected to pressure in one direction, the alteration in form of the paste block will not alter the law of distribution of the particles. In any case, as we have already shown, proximity does not produce any observable effects.

It is surely natural to suggest that the particles acquired some orientation from the pressure, which might well happen, if they possessed shapes which were related in some particular way to their structures. Thomson immediately pointed this out to Tyndall, who replied that if that were the case, the bismuth fragments being naturally in the form of flakes parallel to the cleavage planes, the line of pressure ought therefore to set itself axially, whereas it actually set equatorially. This was certainly a good reply. Perhaps the counter argument is that the crystal fragments have not actually been shown to set in this way. Miss Knaggs has made an X-ray measurement of the set of the fragments in one specimen of squeezed dough containing bismuth particles, and has found that the cleavage planes are not closely co-planar with the surface, as they must be if Tyndall's argument is to be good. Though this is a single example, it looks as if a way of escaping the difficulty was to be found.

As I have said, Tyndall's reply to Thomson was good, but, to use his own words, though it formed "a strong presumptive argument it was not <sup>at</sup> convincing." He strengthened his case greatly by a further experiment. Comparing the repulsion exerted by a magnet on a natural crystal of bismuth with that exerted on a mass of compressed powder in dough he found the latter greater than the former. He had cut the crystal into the form of a cube and placed it on one arm of a torsion balance so that the cleavage plane was perpendicular to the magnetic field, and the repulsive force as great as it could possibly be. The dough had been pressed into a cube of the same size and placed with its line of pressure at right angles to the field. Tyndall argued that there must be a direct effect of pressure, since it had done more than all that the natural phenomena could do.

Now it is clear that if the orientation of a bismuth crystal in a uniform magnetic field, i.e. the magne-crystallic action, is due to the arrangement of the atoms and molecules in the crystal structure, the perfect crystal ought to show the effect more perfectly than the fragments distributed through the dough, however perfectly the latter may be arranged. But Miss Knaggs has made an X-ray photograph from the face of a natural "crystal." The specimen was clipped out of a mass of crystals left in a crucible, and must have resembled that which Tyndall used. The photograph showed at once that the specimen was a compound of more than one crystal, and that different orientations were present. Cleavage planes, and also others which in a single crystal would make large angles with the cleavage planes, were nearly parallel to the face under test. It is possible therefore that there was really more of the effective orientation in the pressed specimen than in the natural piece. A photograph of the single crystal made by Bridgman's method taken in the region of the cleavage plane gave a much cleaner picture.

A piece of bismuth can be looked on as an aggregate of crystals. There may be but one perfect crystal, or there may be a number, small or large, of smaller crystals, each perfect. If proximity were increased by pressure, the change in proximity would have to occur in respect to the mutual distances in either of the separate crystals, or of the atoms and molecules in the single crystal. The X-ray analysis shows that the latter alternative is impossible because from many tests recently carried out in respect to metal structure we learn that no permanent change in the crystalline lattice is occasioned by stress. The former alternative is also ruled out, because as Faraday pointed out\* bismuth is actually of a lower density after compression than it was before; the pressure having of course been removed. Apparently the breaking up of the specimen increases the extent of the cavities.

Tyndall made many paste models of crystals, mixing powders of bismuth, carbonate of iron, or other active substances with flour and water, or gum. He pressed the mass by different amounts in different directions and then cut it to shape; in this way he imitated the magne-crystallic action in detail. At one time, in order to meet the objection that he was merely rearranging the small crystals in his paste and conglomerates, he took some white wax "concerning whose amorphism there can be but little doubt." The substance is diamagnetic. A little cylinder of the wax suspended in the magnetic field set with its axis equatorial. It was then placed between two stout pieces of glass and squeezed as thin as a sixpence; suspended from its edge the plate thus formed set so that its length, which coincided with the axis of the previous cylinder, was axial and its shortest dimension equatorial. But we know now that wax is anything but amorphous; its crystalline structure has not only been observed but accurately measured; and we know also that pressure arranges the orientation of the crystals.

He obtained the same result with a piece of bread, and we may repeat the experiment. A small piece of the crumb is squeezed between two glass plates, and the edges of the irregular mass are trimmed off, so as to leave a thin disc. When this is suspended so that its plane is vertical it sets equatorially if the poles are close together and the field is very divergent. It is therefore diamagnetic. But when the bread is moved from the space between the poles to a more uniform part of the field, the plane of the disc turns through a right angle and sets itself parallel to the lines of force. It is quaint to observe how the bread, as it is moved up the poles, sets itself to pass neatly through the narrow gate and take up a parallel position on the further side. This is due to magne-crystallic action, so that the bread contains crystals, a fact easily verified by X-ray methods.

\* His reference was to Gmelin's "Handbook of Chemistry," iv. 428.



The long series of interesting and ingenious experiments which Tyndall made to show that pressure produced proximity, and proximity produced the equivalent of magne-crystalline action, must be held to have failed in their original purpose. But they will doubtless be put to a different use. They are related to a subject of immense importance in these days—namely, the effects of pressure, and tension and mechanical treatment generally upon the state of a material and upon its physical properties. The consideration of such questions is fundamental to metallurgy and to other great industries. The microscope has for many years been employed for the purpose, and the new methods of X-ray analysis are already being put into service. It may well repay us to consider Tyndall's experiments in a new light; and to examine the actual nature of those rearrangements which produced such remarkable changes in magnetic

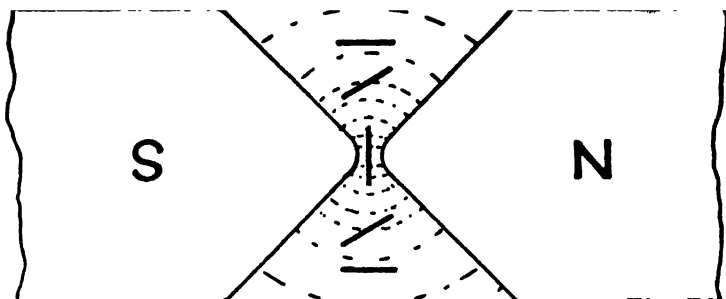


FIG. 9.—The black lines show different positions of a thin wafer of pressed bread hung by a single fibre. In the outer parts of the magnetic field it sets more or less along the lines, but as it is brought up to the more intense parts where there is great divergence of the lines it turns so as to set itself at right angles to the field.

reactions. Tyndall himself discussed the effects of pressure in producing planes of possible cleavage, and was one of the pioneers in showing how such planes, occurring in the earth's crust, were not always to be interpreted as the result of sedimentary deposition, but rather of pressure, which might, if it were exerted more or less along the deposition planes, produce cleavages across the latter. He extended the principle to account for stratification in rolled materials, even in biscuits and pastry.

Faraday's use of lines of force did not, in reality, demand so much framing of hypothesis as Tyndall's polarity. It is to be observed that, as Faraday pointed out, they had no differences about facts, merely about methods of description, which methods, however, were of different value as suggesting development. To Faraday's conceptions have been added theories of magnetism and diamagnetism

based on the existence of resistanceless molecular circuits as imagined by Ampère and Weber, or on revolving electrons as explained by Langevin. In the most recent times the quantum theories have again modified our ideas.

The crude hypothesis of the molecular circuit leads simply to a useful point of view of the difference between paramagnetism and diamagnetism, and the most modern discussions though they differ greatly in appearance leave that point of view almost untouched. If any of Faraday's lines of force thread a circuit which has no electrical resistance, that number can never be changed. If, therefore, a substance be brought into a magnetic field, the molecular circuits in the atoms of the substance act like obstructions to the lines, and the total obstruction, of which the negative magnetic susceptibility is a measure, is proportional to the sum of the areas of all these circuits, as projected on a plane perpendicular to the lines. It is of no consequence whatever whether there are already currents in those circuits; unless indeed the circuits are movable and can alter their set towards the imposed field. Thus the diamagnetism is unaffected by the existence of molecular magnetic fields; or by any changes in them, so long as the total of the projected areas of the circuits is unchanged. This result does not hold if circuits approach each other so closely that they offer less obstruction to the lines than if they were more separated. Two resistanceless circuits running closely parallel to each other offer little more opposition to the passage of lines than either circuit alone. We should imagine that such changes in the relative position of circuits would only occur under strenuous circumstances such as possibly those of crystallisation. It is known that diamagnetic susceptibility may vary very slightly; for instance, Oxley has shown that crystallisation sometimes brings about small but definite alterations. As has often been pointed out, this simple theory makes diamagnetism a property of all substances, which can be affected, even overwhelmed, when the circuits already contain currents, and therefore can be orientated afresh by the magnetic field.

Let me say in conclusion that although recently acquired knowledge of the structure of materials leads us to reconsider Tyndall's experimental results, we are still far from the full explanation of the connection between structure and magnetism, and of the influence of the latter upon physical properties.

[W. H. B.]

Friday, March 4, 1927.

SIR ROBERT ROBERTSON, K.B.E. M.A. F.R.S., Secretary and  
Vice-President, in the Chair.

SIR HERBERT JACKSON, K.B.E. F.R.S. M.R.I.,  
Director of Research, British Scientific Instrument  
Research Association.

### Some Colouring Agents in Glasses and Glazes.

THE colouring agents of glasses and glazes are very many; moreover, several of these agents can impart colour to glasses or glazes in what may be described as different ways. An explanation which would include all our present knowledge of the behaviour of any one of them would occupy a long time. I have chosen two colouring materials, copper and iron, and hope to deal with some of the effects which can be produced by them and their compounds. If time permit I should like also to make a few remarks on certain effects which can be produced by radiations such as ultra-violet light, X-rays, and gamma-rays from radio active materials.

I have chosen copper and iron because, in their various modes of action as colouring agents in glasses and glazes, they illustrate fairly completely the manner in which most of the materials used in this connection behave. For our purposes this evening I will not draw any definite distinction between glasses and glazes, but will use the terms somewhat indiscriminately.

Copper can be introduced into a glass or glaze so as to produce reds, browns, yellows, greens, blues, purples and black. In some instances the colours can be well seen by transmitted light, in others the material is too opaque to show the colour except by reflected light. These various effects are produced by compounds of copper or by metallic copper itself. Of the compounds of copper, attention will be especially devoted to the two oxides of copper, cuprous oxide and cupric oxide. Cuprous oxide is the colouring agent in the brilliant scarlet Egyptian glass, specimens of which appear to be correctly attributed to at least as far back as the XVIII. Dynasty and up to Roman Egyptian times. It would appear from the absence of any specimens attributable to more recent times that the knowledge of how to produce this glass successfully was then lost.

Microscopic examination of a specimen of the scarlet Egyptian glass given to me some years ago by Professor J. N. Collie, and of other

specimens given to me more recently by Mr. Horace Beck, showed that the colour was due to small crystals of cuprous oxide. Chemical examination of the glass itself revealed that it was an ordinary lead glass containing about 30 per cent. of lead oxide, and the quantity of cuprous oxide varied from about 8 per cent. to 10 per cent. Based on this information the glass was successfully made after a few trials. During those trials yellow crystals were often observed in parts of the glass, and recently Mr. Horace Beck provided me with an orange yellow bead found at Faversham, in Kent, the colouring matter of which was again identified as cuprous oxide, but mainly in the yellow form. The red form of cuprous oxide is the better known form, and is produced when copper is heated in a limited supply of air: it can generally be well seen on the underside of the black scale detached from a piece of metallic copper which has been heated for a short time to a high temperature in air and then kept at a lower temperature for some time.

A ready method of producing the red oxide is to add a solution of copper sulphate to a solution of glucose and then to add caustic potash to the mixture. On heating the clear blue solution so obtained, reduction of cupric oxide by glucose occurs, with consequent precipitation of red cuprous oxide. At the first stage of heating it is generally possible to notice the formation of a yellow precipitate mingled with the red; these colours can be better shown by using Fehling solution, which is made up from copper sulphate, Rochelle salt and caustic potash, and is a clear blue solution. If a small quantity of the solution of glucose be poured into a large quantity of boiling Fehling solution the red oxide is formed. If a small quantity of Fehling solution be added to a large volume of boiling solution of glucose, the yellow form is produced, and is permanent in the sense that it may become rather more orange in tint but does not reach the red stage.

Without going into the doubtful composition of this yellow form, in respect of the extent to which it may be considered hydrated, it may be remarked that if it is heated out of contact with air the yellow form persists, and is apparently completely freed from water at a temperature of about 350 °C. The difficulty of making any statement about the temperature at which the yellow form can exist in glass will be appreciated if a short description is given of the behaviour of cuprous oxide glass during its preparation.

If the proportion of cuprous oxide introduced into the glass be about 8 per cent., the whole of it dissolves in the glass at the temperature of 1000 °C. at which the glass is made. If the glass be quickly chilled from this temperature no colour, except the almost unavoidable green colour due to oxidation of part of the copper, will be seen; the glass is a nearly colourless transparent one. On re-heating this glass it is possible to produce, according to the temperature to which the glass is raised and the length of time

during which it is heated, comparatively large crystals or aggregations of crystals of red cuprous oxide, smaller crystals of the same form, or particles so small as not to be recognised as crystals under the microscope. Along with these are frequently obtained definite crystals of the yellow form, clouds of yellow particles, and, if the re-heating be gentle, the particles of yellow cuprous oxide are so small as to be unrevealable by the microscope, and what is obtained is a clear yellow transparent glass. Here then, from two forms of one and the same oxide of copper, we have a range of colours associated with the proportions in which the two forms are mixed in the glass and with the size of their particles. What is the inner nature of the difference between the red and yellow forms which may account for their difference in colour is yet to be made out.

Much ancient Egyptian glass does not contain lead, but is mainly of the composition of an ordinary window glass—that is to say, its principal ingredients are silica, lime, soda, with varying quantities of potash, magnesia and alumina. It has not been found possible to make the brilliant scarlet cuprous oxide glass satisfactorily in a glass of this composition. The temperature required for the proper making of such a glass is too high for the persistence of the scarlet colour, and the resulting glass is of a brown or brownish red colour. A scarlet coloured glass of the common soda-lime type could be made if the composition of the glass were so chosen that its fusing point was as low as that of the lead glass which the Egyptians used. If the Egyptians ever did make such a glass, it would have been so unstable that it could hardly be supposed any specimens of it would have persisted to the present day.

Ancient brown glass of the soda-lime type just referred to appears to have been very widely distributed. Recently I have been given some beads of this glass which, I am informed, work up through the sand on the coast of Zanzibar. Whatever attribution is given to the various specimens, they all seem to be very similar in composition and to depend for their colour upon the presence in the glass of minute particles of metallic copper. Whether the production of this brown or brownish red glass preceded that of the scarlet glass is a question which cannot be dealt with here. It is worth while, however, to refer to one property of cuprous oxide. This oxide does not form salts with acids except with the halogen acids: hydrofluoric, hydrochloric, hydrobromic and hydriodic. With the oxygen-containing acids, if it re-acts with them, metallic copper is produced along with a cupric salt of the acid. With sulphuric acid this change takes place at the ordinary temperature: with a weaker acid like acetic acid the action is very slow unless the temperature is raised. Taking these reactions as analogous to what may occur in a glass, and considering silica as a weak acid, it will be understood that if the temperature of a glass, either the lead glass or the soda-lime glass, be raised high enough the result will be the production of

metallic copper dispersed through a greenish cupric oxide glass. If the percentage of cuprous oxide used were high, about that used for the scarlet glass, there would be sufficient green to make the red of copper look, by reflected light, distinctly brown. With less copper present the colour would get nearer to a red, and it will be easily understood how, by using progressively less and less copper it would be possible to arrive at a glass resembling the well-known red glass which owes its colour to particles of copper so finely comminuted as to render the glass quite transparent to the eye. The transparent red copper glass and the brilliant *sang de bœuf* Chinese glazes are made under conditions which tend to reduce any cupric oxide which may be formed, so that the resulting glass is not rendered dingy by a green tint, due to dissolved cupric oxide, marring the brilliant red due to the dispersed metallic copper. It should be added that for this brilliant glass so little copper is used (it is in the neighbourhood of 0.5 per cent) that any colour from cupric oxide which would arise from such a change as is mentioned above under the action of silica would be so pale as to have practically no effect on the brilliance of the red due to the dispersed copper.

Here then again we have considerable variations in the appearance of the glass dependent upon the size of the particles of the colouring agent dispersed through it, and this is made evident when thin pieces from different portions of glaze from one and the same Chinese *sang-de-bœuf* vase are examined by transmitted light. Under the microscope, for example, some pieces are distinctly red, others are purple, others again are blue, and others look like neutral coloured glass. Closer study shows that in the most brilliant red portions no particles can be seen by the microscope. In some of the less transparent red pieces, particles are revealed either by a cloudiness or as discrete particles. In the purples these particles are larger, and in the blues they are still more marked, while in the neutral colours the particles are generally seen less closely packed but distinctly larger in size.

The colours produced by cupric oxide in glasses and glazes need not be dealt with in detail as there is much common knowledge about these. One or two points not in common knowledge may however be emphasized. In a glass of the same composition cupric oxide may give a very marked blue colour if the glass is made at a comparatively low temperature (1000°C. to 1100°C.); whereas with the same concentration of copper and the same glass made at a higher temperature, about 1300°C. for instance, there is a very marked green shade in the blue. It is worth pointing out that the blue low-temperature glass is green while hot.

It would lead us into too much detail to do more than call attention to the possible analogies between the action of water in solutions of cupric salts and the action of the oxides of the alkali metals in glasses coloured by cupric oxide. The change from blue

to green just mentioned in the case of the low-temperature cupric oxide glass calls to mind the fact that a green solution of cupric chloride which becomes blue when sufficient water has been added becomes green again on heating it. A study of the changes of colour which can be produced in aqueous solutions and salts, and of the methods of modifying these colours, has been of great assistance to me in shortening the experimental work necessary to arrive at the compositions of a number of glasses in which it was desired to produce certain colours either with copper or other colouring agents.

As an example of the change of colour effected by adding water to a salt, copper sulphate may be mentioned. This salt, in its anhydrous condition or with only one molecule of water, is colourless. Crystals containing five molecules of water are the ordinary blue copper sulphate crystals, and the solution of these in water is blue. If we take boric anhydride and an oxide of an alkali metal as analogous to sulphuric acid and water, a very similar story can be told. A small quantity of cupric oxide does not dissolve in fused boric anhydride, but forms a white borate which is dispersed through the fused mass. The addition of an alkali will bring about solution and give a clear blue transparent glassy mass. The most striking example is to take boric anhydride and the alkali lithium oxide in, say, three different proportions, such as one molecule of lithium oxide to one of boric anhydride, 1 to 4 and 1 to 10. With 0.5 per cent. of cupric oxide the first is a fine deep blue; the second is a paler blue; the third is still paler; and if the proportion of alkali oxide be lowered until there is only just sufficient to bring about complete solution of the cupric oxide in the mass, there is but little colour to be seen at all.

With many glasses made at a high temperature, cupric oxide gives an olive green colour. Without going so far as to say that the dusky shade in the green is invariably due to some reduction of the cupric oxide to the lower oxide of copper, there is evidence of this in certain instances which I have come across. To take one: in making trials for a glass which was intended to be of a green colour with only a slight tinge of olive in it, and of a sufficiently light shade to enable the light of a candle flame to be seen through a 1-inch thickness of the glass, the furnace conditions happened to change on one occasion so that the glass was exposed to a reducing atmosphere. The resulting glass was so black that a bright June sun was invisible through a piece of the glass one-fortieth of an inch thick. Such a state of affairs might be considered to come about by the glass being a mixture of red copper glass mixed with a green cupric oxide glass, through which mixture but little light could be transmitted. Now red glass owing its colour to finely dispersed metallic copper is rendered colourless by fusing it and quickly chilling it. The black glass referred to might, therefore, be expected to become green if fused and quickly chilled, but it did not change

from its intense black colour. This just gives a hint of the possibility of a cuproso-cupric compound being present in the glass analogous to, though not so definite as, ferroso-ferric oxide, the well-known black iron scale. Again, an analogy with solutions helps a little. If to a colourless solution of cuprous chloride in hydrochloric acid there be added a transparent green solution of cupric chloride the mixture turns black. Although dusky greens and the black glass just referred to might be accounted for by varying mixtures of red and green glass the colour of this solution could hardly be accounted for in the same way. Moreover, in experimenting with red copper glasses, and studying the way in which the red colour can be prevented from developing by sudden chilling and can be produced by subsequent heating, I have repeatedly noticed that, instead of obtaining a clear colourless glass in bulbs made from the red glass and quickly chilled, the bulb has been sometimes of a dusky hue and sometimes of a definite neutral tint. As no other colouring agent but copper was present in these glasses I am inclined to attribute the neutral shade to a cuproso-cupric compound which is stable in the glass, and which is analogous to the compound formed when the cuprous and cupric chloride solutions are mixed, rather than to a physical mixture of red and green glasses.

I must not deal further with cupric oxide glasses except to mention that, unlike cuprous oxide glasses, copper glasses and many other coloured glasses, such as gold glasses, selenium glasses, cadmium sulphide glasses and opal glasses, cupric oxide glasses cannot be rendered colourless by sudden chilling, nor, indeed, can the tint of these glasses be modified to any noticeable extent in this way. An attempt to explain this difference, which seems to divide colouring agents generally into two classes, would involve a very lengthy account of the various phenomena which have been observed, and would, moreover, be to a considerable extent little more than a re-statement of facts which would involve differentiation between the meanings of such terms as "solution," "chemical combination" and "dispersion," and would lead to much argument. I must content myself with this short and incomplete account of the modes of behaviour of copper and its oxides in glasses and glazes.

Passing on now to iron, there are colours produced by ferric oxide, ferroso-ferric oxide and ferrous oxide, but I do not know of any glass or any material which could be called glassy which owes its colour to metallic iron in a fine state of dispersion. Starting in the first place with ferrous oxide, which gives the well-known green colour to glass of the nature of window glass, I need only point out that this colour is considerably modified by the composition of the glass, and without going into a number of details I will mention the way in which this tint is modified by the presence in the glass of zinc oxide or magnesium oxide. The former intensifies the colour



produced by any given amount of ferrous oxide and changes the usual green into almost a blue. A similar change occurs with magnesium oxide, but the intensification of the colour is less marked. Among the alkalis, lithium oxide also tends to give a bluish tint to glasses containing ferrous iron. A notable example of this is seen in an early Chinese glaze which, through the kindness of Mr. G. Eumorfopoulos, I had the opportunity of examining. The thinner parts of this glaze are practically colourless, but the thicker parts have a beautiful blue tint. An examination of the glaze showed that it was for such glazes unusually rich both in lithium oxide and in magnesia, and the colouring material was identified as iron. If the Chinese workers had substituted zinc oxide for the magnesium oxide in their glaze mixture the colour would have been very much more marked.

Before dealing with the colours and effects produced by ferric oxide in glasses and glazes let me call attention first to the different shades of colour which can be seen in varieties of the oxide itself. These range from a reddish yellow through brick reds, bright reds to a rich brown-red and almost to a black. Some specimens also have almost a bronze-like appearance. The range of colours produced when ferric oxide is used as a colouring agent for glasses and glazes is practically as great. It is doubtful if the colours produced by ferric oxide are due to compounds of this oxide with the other constituents of the glass. Without going into elaborate detail it is somewhat difficult to give adequate support to this statement. Perhaps the simplest way of dealing with it is to take the behaviour of ferric oxide in lead glasses, frequently described as flint glasses. There are light flints and dense flints. In the light flints there is always a notable quantity of an alkali such as potash or soda along with the lead oxide. In the dense flints the proportion of alkali is decreased and the proportion of lead oxide is increased. Now, taking three such glasses for example, having specific gravities of 3.2, 3.8 and 4.8, it is possible to add a known, but small, quantity of ferric oxide to the first glass and still to produce a glass having no detectable yellow colour to the eye. The same amount of iron added to the second glass will give a noticeable yellow colour, and added to the third glass will give a marked yellow colour. The glass of specific gravity 3.2 contains a notable proportion of alkali, and there is reason to believe that this either promotes the formation of a compound of ferric oxide with the alkali or the formation of a double silicate, either sodium ferric silicate or potassium ferric silicate; such compounds appear to be colourless. If the quantity of iron be increased, then a colour can be produced in the light flint, and, by increasing the percentage of ferric oxide to 5 per cent., a fairly strong yellow colour is produced. With 10 per cent. of ferric oxide in the same glass the colour is a deep brownish red when looking through a thickness of about 3 mm. With 20 per cent. of ferric

oxide an even richer red colour can be seen when looking through a thickness of  $\frac{1}{2}$  mm.; but in thicknesses of 1 mm. or higher the glass is practically opaque. When the percentage of iron is raised much higher, some ferric oxide crystallises out from the glass on cooling, and with 40 per cent. of ferric oxide the small crystals dispersed through the glass can be seen with a hand lens. With the denser flints, containing a lower percentage of alkali, colours similar to those described above are produced with much smaller proportions of ferric oxide.

A reasonable explanation of this would be on the same lines as the suggestions made in dealing with cuprous oxide and metallic copper, viz. that the light yellow colour is due to a small amount of free ferric oxide dispersed in the glass as extremely fine particles; the transparent deep yellows and brownish reds would represent a greater concentration of ferric oxide similarly dispersed, possibly also, as the percentage of ferric oxide gets higher, as somewhat larger particles. In the 20 per cent. glass mentioned the particles are still too small to be seen, but in specimens of lead glass containing nearly 30 per cent. of ferric oxide fine clouds of almost irresolvable particles can be seen in the microscope.

Leaving the subject of lead glasses coloured with ferric oxide, I would first mention the behaviour of ferric oxide in a glass containing a large proportion of phosphoric acid, an acid which in glasses may be described as a much stronger acid than silica. Ferric phosphate is a definite compound and is colourless; in this phosphoric acid glass, quite a notable proportion of ferric iron may be present without showing any colour. Evidence that the iron is in the ferric state is obtained by heating the glass in a highly reducing atmosphere; this reduces the ferric iron to the ferrous state, and the glass is found to have developed a marked indigo blue colour, due, possibly, to ferrous phosphate, or to ferrous phosphate along with a very small proportion of unreduced ferric phosphate.

In such glasses as ordinary sodium calcium silicates it is rather difficult to obtain light pure yellow colours with ferric oxide. Much use has been made of ferric oxide in producing glazes which are of a deep colour: practically black in moderately thick layers, though of a fine golden brown in thinner layers. These glazes are frequently described as felspathic glazes, and their composition may be given as sodium or potassium calcium aluminium silicates. To get the deep colour of these glazes, amounts of ferric oxide of the order of about 12 per cent. are required. If the percentage of ferric oxide is raised to about 15–20 per cent. some of the ferric oxide separates out on cooling and, according to the concentration of the ferric oxide, so may be seen a fine brown red colour on the surface of the glazes or bronze-like spangles of ferric oxide, or rosettes, or tree-like crystals, or even more massive crystals which to the eye look black. The Chinese made much use of this behaviour of ferric oxide. As the

result of a close microscopic study of certain Chinese glazes owing their colour to ferric oxide, which I undertook in collaboration with Mr. A. L. Hetherington, he was able to explain how the varied and beautiful effects seen on certain specimens of Chinese porcelain could be obtained, and to show many similar glazes produced in the laboratory to support the explanation put forward.

Ferroso-ferric oxide, magnetic oxide of iron, gives in certain glasses neutral tints of various depths, but with high concentration of this oxide a black glass can be obtained. If the concentration of the ferroso-ferric oxide be high enough, some of this oxide will come out on cooling so as to be dispersed through the glass in very minute aggregations which are, however, presumably crystalline since the resulting glass is appreciably magnetic. The above remarks refer to glasses containing the whole of the iron in the ferroso-ferric form. If a ferrous iron glass or glaze contains some ferric iron, the green colour due to the ferrous iron will be modified and various olive green tints can be obtained. There are many such coloured glazes in which the iron is principally in the ferrous state, but there is sufficient of the ferric iron present to produce the olive green tint. In a similar way small quantities of ferrous iron in a glass which contains appreciable quantities of ferric iron will modify the yellow or brown colours due to the ferric iron and give somewhat dusky hues.

Before leaving the subject of iron I am tempted to hazard a guess at the nature of the colouring matter in lapis lazuli. In almost all the specimens which I have seen, here and there crystals of iron pyrites (ferric sulphide) can be seen. An examination of these specimens under the microscope reminds me very strongly, except for the difference of colour, of the appearances of many of the glazes very deeply coloured with ferric oxide in which also crystals of ferric oxide can be seen. The colouring of lapis lazuli is very intense, so much so that very thin portions of it make equally thin portions of the deepest blue glass obtainable look almost white by comparison. Let me for a moment call attention to a simple experiment with solutions. If to an aqueous solution of ferric chloride, as free as possible from free hydrochloric acid, there be added quickly an aqueous solution of hydrogen sulphide, there is the production of a transient intense lapis lazuli colour. It has been suggested that this colour is due to the formation of a ferric sulphide which, in the solution, rapidly breaks down to a ferrous salt with the separation of free sulphur. My guess in respect of lapis lazuli is that the beautiful blue colour is due to minute particles of ferric sulphide, altogether too small to be seen by the microscope, dispersed through the mineral. Different concentrations of the dispersed ferric sulphide would account for the various lighter blues, full blues and dark, almost black, blues which can be seen in specimens of lapis lazuli. I hope to be able to find a specimen of lapis lazuli of the

very blackest blue colour obtainable and to examine it critically by the microscope; I also hope to be able to test the suggestion made, by synthetic experiments.

I should mention that, in the process of making artificial ultramarine by heating together clay, sodium carbonate, sulphur and charcoal, or some other substance rich in carbon, it has been stated, I believe, by a number of experimenters that small amounts of iron must be present in the materials. I need hardly mention that almost every clay contains small, but appreciable, quantities of iron.

I have only time to deal with a few points about the third colouring agent which I mentioned at the beginning. It is quite a common thing to see glass in windows which by long exposure to sunlight has developed colour ranging from a pink, through various depths of rose-violet almost to a marked blue-violet. Some window glasses also become coloured with a brownish-yellow tint by long exposure to sunlight, but the colour is not usually noticeable. By the kindness of Dr. G. C. Simpson I am able to show a glass sphere taken from a sunshine recorder. The originally colourless or slightly green glass has become a pronounced yellow-brown; the colour of this sphere is very marked in comparison with the colourless sphere shown alongside it.

The colour developed in a glass by exposure to sunlight is partly determined by the composition of the glass. Similar discoloration can also be produced in glasses by exposing them to ultra-violet rays of shorter wave-length than those present in sunlight, to X-rays and to the radiations from radium, but the colour developed by these agencies is not, in every instance, the same as that which can be produced in the same glass by exposure to sunlight. There can be little doubt that the radiations are the cause of the colour, though what is the nature of the material which is separated out by the action of the radiations, and which produces the colour, is not fully known. In purpled window glass, manganese has been frequently mentioned as the colouring material, it being sometimes assumed that under the influence of the radiations the colourless manganous oxide in the glass becomes oxidised to a purple manganese peroxide. In a similar way it has been suggested that the brown colour such as is seen in the sunshine sphere is to be explained by the oxidation of the ferrous iron to the ferric state. There are certain difficulties in accepting these explanations of the colours. The colourless sunshine sphere shown was, a few weeks ago, a much darker yellow-brown than its companion which shows the marked brownish-yellow colour. Both spheres were colourless when new, and the present colourless one has been rendered so by heating it to a temperature of 500° C. All the varieties of coloured glass with which I have been able to experiment, and which owe their colour to the action of radiations, can similarly be decolorised by heating to an appropriate temperature; but of all the glasses I have tried which have

been purposely coloured by ferric oxide, or by manganese dioxide, I know of no example which can be decolorised by heating, even if it is heated up to a temperature sufficiently high to re-melt it. This is not to say that these observations refute the suggestions of the nature of the colour mentioned above, but they certainly introduce difficulties which it would take too long to elaborate on this occasion.

Just as glasses can become discoloured by radiations so have many minerals apparently been similarly affected, and in all examples which I have tried, and in which the colours were produced presumably by radiations, the colouring could be discharged by heat. Highly coloured fluor spar is a typical example: purple amethyst, smoky quartz, rose quartz, yellow quartz, and various coloured zircons, known in the gem trade as jargons, are others. All of these can be decolorised when heated to an appropriate temperature. A fine purple amethyst, for example, became clear colourless quartz at a temperature of about 400 °C. A rather browner purple amethyst lost its purple at the same temperature, but had a yellow colour left, which was discharged however at 700 °C., and the resulting quartz was white but not clear: it was opalescent.

In all the instances mentioned above it is found that when the colour of the glass or mineral is discharged by heat the apparently colourless material shows a marked absorption in some part or other of the ultra-violet spectrum.

In the instances of glasses and fluor spar it is generally found that the decolorised specimens exhibit marked fluorescence under the influence of ultra-violet light. I have not seen examples of crystalline quartz which show similar fluorescence, but if the decolorised amethyst be fused, the vitreous silica so obtained shows marked fluorescence. Either the decolorised amethystine quartz or the same substance fused can be coloured again by exposure to radiations, the colour being developed most readily by exposure to the gamma-rays of radium. It is not possible, with pure crystalline quartz, which shows the highest transparency to ultra-violet radiations, to produce any coloration by submitting it to the action of the gamma-rays from radium over a period sufficient to produce marked coloration in the decolorised amethyst or in decolorised rose, yellow, or smoky quartz. Similarly I have not found it possible with fluor spar of the highest transparency to ultra-violet light to colour it by gamma-rays, but there are many specimens of fluor spar colourless to the eye which fluoresce in the ultra-violet light, and these can be coloured by exposure to the gamma-rays from radium.

From all the observations it certainly seems that the substances I have mentioned owe their colour to the action of radiations, and become coloured only when they contain a small quantity of a suitable impurity. There is no conclusive evidence of the exact nature of the material which, separated out by the action of the radiations, imparts colour to the glass or mineral. Finely dispersed

metal such as calcium has been thought possible as accounting for the colouring of glass, fluorspar and Iceland spar, but glasses which contain no calcium become coloured by radiations, and it is not impossible to imagine finely dispersed potassium or sodium as the colouring material. Silicon itself has been suggested as producing the colour of some quartz, and so has titanium, and so has carbon. It is difficult to see why silicon, which is made to go back as silica by heating, should render the quartz opaque to some ultra-violet radiations. There is no suggestion which has been made which is not open to some objection or other.

In the production of these colours there appears to be some analogy with the ordinary changes which are observed in silver salts on exposure to light. A pure silver halide (chloride, bromide, iodide) is apparently unaffected by light. That the well-known action of light on these compounds as they are generally prepared is ascribable to the presence of small quantities of some other material or material<sup>s</sup> is generally accepted; but no one would suggest with our present knowledge that the dark material which develops in the silver salt when exposed to radiation consists of the impurity. The darkening is ascribed to decomposition of the silver salt, which decomposition is rendered possible by the presence of the impurity.

Taking into account all the observations which have been made on the effect of exposing various glasses and minerals to radiations and to cathode discharge, it would appear not unlikely that the colours produced in these experiments are ascribable to the separation from the material of one or other of its constituents by the action of the radiation, which separation is only possible provided there is present in the material a suitable impurity; but change the line of argument a little, and there are facts which would appear strongly to support the view that it is the impurity itself, in many instances, which becomes separated out in a fine state of division by the radiations and which imparts the colour to the glass or mineral. We do not know. There is a mass of evidence to be considered, but much more experimental work is needed before that evidence can be dealt with and properly assessed.

[H. J.]

Friday, March 18, 1927.

SIR ROBERT ROBERTSON, K.B.E. M.A. F.R.S., Honorary Secretary  
and Vice-President, in the Chair.

EMIL HATSCHEK, F.Inst P., Lecturer on Colloids,  
Sir John Cass Technical Institute.

### Rigidity and other Anomalies in Colloidal Solutions.

As the term "rigidity" has colloquial and metaphorical connotations it may be advisable to begin by defining the strict technical meaning of the term. If we consider a cube of an elastic solid fixed with two opposite faces to two parallel planes, one of which is immovable, while a tangential force is applied to the other, the cube undergoes a deformation which is called "shear." It resists it by virtue of a property called its "rigidity," which causes it to return to its original shape, as soon as the force or stress ceases to act (Fig. 1).

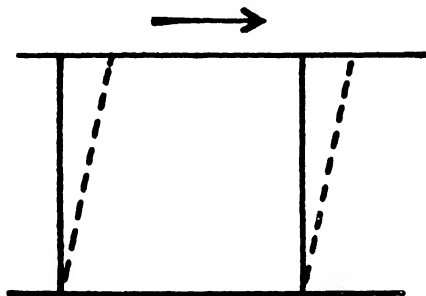


FIG. 1.

In a transparent isotropic material, such as the gelatin jelly which is being shown, a further change can be observed when the deformed body is viewed in polarized light: it becomes double refracting, and this shows itself in the familiar manner by the appearance of interference colours. This accidental double refraction, as it is called, is a very delicate means of detecting strains in transparent media, and can be used for determining their distribution and magnitude.

We can deduce a quantitative measure of rigidity from the terms of the experiment shown: the so-called modulus of rigidity, which

is the force that, acting on a cube of unit dimensions, would produce unit deformation. The modulus of rigidity of steel is of the order of tons per sq. cm., that of the gelatin jelly which has been shown is about 100 grm. per sq. cm.

It must be added that the rigidity of a perfectly elastic material does not vary with the time; if a given deformation is to be maintained, the stress necessary to produce it remains the same however long it is applied.

Rigidity is one of the most characteristic properties of the solid state, and absent in all normal liquids. We can best realise the difference between solids and liquids in this respect by considering what is now merely an ideal case: two indefinitely extended parallel planes, between which a liquid is contained. If now a force, however small, is applied to one plane, while the other is kept fixed, it moves, not only a small distance as with the elastic solid, but continuously as long as the force acts, and comes to rest as soon as it ceases to do so. The force required to maintain a certain velocity is proportional to the area of the plates, the velocity gradient, i.e. the velocity of the moving plate divided by its distance from the fixed one, and depends on a property of the liquid called its viscosity. A quantitative expression again suggests itself from the conditions of this mental experiment: the force per unit area required to maintain unit velocity when the plates are unit distance apart; this is called the viscosity coefficient. In all liquids it decreases rapidly with rising temperature.

A very remarkable feature of this physical constant is that in all normal liquids it is quite independent of the velocity with which they are being sheared; if all else is kept constant, the forces required to maintain two different velocities are exactly proportional to these velocities. The proof of this constancy of the viscosity coefficient is both indirect and direct. The mathematical theory, e.g. that of the measuring devices, has been developed on the assumption of a constant viscosity coefficient, and the results agree with experiment. The viscosity of water has been measured by a number of observers over a range of velocity gradient varying in the ratio of 1 to 10,000, and has been found quite constant.

Instead of expressing the viscosity coefficient in the absolute units of the definition, it is customary in work on solutions, such as we shall consider, to express it as "relative viscosity," the viscosity of a standard liquid, generally the solvent itself, being taken as unity. Thus the relative viscosity of a 60 per cent. solution of cane sugar at 20° is 56.5.

Since, as we have seen, a normal liquid yields at once to the smallest force, no deformation like that in an elastic solid can be set up in it, nor of course the accompanying phenomenon of double refraction. Experiments with the object of detecting whether accidental double refraction could be produced in liquids by shearing



them very rapidly have been made by a number of physicists, beginning with Kundt in 1881. He confined the liquid in a narrow annular space between two coaxial cylinders, one of which was rotated rapidly, and examined it in polarized light. No effect could be detected except in a few liquids which we now know to be colloidal solutions of a special type.

The arrangement of two parallel planes with liquid between them, which we have been considering, is hardly realisable experimentally, but we can, without materially affecting the reasoning, so to speak roll up the two planes, and confine the liquid between two concentric cylinders, the outer of which is rotated while the inner is at rest. This arrangement, to which we shall refer again, can then be used for determining viscosities over a great range of velocity gradients.

Historically this is not the first device used for such measurements. The systematic study of viscosity began with the work of Poiseuille, who, in 1842, found empirically the law governing the flow of liquid through a capillary tube. This "transpiration method," as it was originally called, has been very largely used since for determining the viscosity coefficients of all kinds of liquids. Thomas Graham, the founder of colloid chemistry, applied it to colloidal solutions, and was greatly struck by the changes in viscosity which they exhibited on ageing, or on addition of electrolytes, so that in his famous paper of 1863 on Silicic Acid he made the, often quoted, remark that "a liquid transpiration tube may be employed as a colloidoscope."

The transpiration tube or, as we now call it, the capillary viscometer, was subsequently used by a large number of observers, generally in the simple form given it by Wi. Ostwald, in which the pressure causing the flow is produced by a column of the liquid itself. It became evident, as measurements accumulated, that colloidal solutions did not behave like normal liquids, but the continued use of the capillary instrument produced no enlightenment, and, for theoretical reasons which need not be discussed, is inadequate to do so. On a somewhat different level is an investigation by Garrett, which forms the subject of a Heidelberg dissertation published in 1903. He studied the viscosity of various colloidal solutions both in the capillary and by a method not used before, that of the oscillating disc. If a circular, horizontal disc suspended from an elastic wire is made to oscillate round its axis in a liquid, the viscosity coefficient of the latter can be deduced from the damping effect by somewhat difficult mathematics. Garrett found in this way that colloidal solutions exhibited a number of bewildering anomalies. The viscosities found by the disc method did not agree with those obtained by the capillary; they were not consistent even by the disc method alone, but varied with the amplitude of the oscillations, and they altered during the duration of the experiment. This disserta-

tion is quoted extensively in all the text-books published about 1910 to illustrate the complexity of the subject, but no very definite attitude towards the problem is taken by the authors.

The first deliberate attempts to bring some light into the matter were made about this time by Professor W. R. Hess of Zürich, the well-known physiologist, and by myself, working in ignorance of each other. Hess had been driven to investigate the problem from practical reasons: measurements of the viscosity of blood and serum had become a clinical method, but various observers had obtained quite irreconcilable results. Hess showed in an improved capillary viscometer that the viscosity of blood and of some colloidal solutions like gelatin was not a constant but varied with the velocity gradient; the faster the liquids were sheared, the less viscous they appeared, until above a certain velocity the viscosity coefficient became a constant.

I published early in 1911 a theoretical paper in which the behaviour of a system having the constitution which was then ascribed to colloidal solutions was investigated. The conclusion reached was that such a system would have a variable viscosity which should become constant above a certain velocity gradient. I then proceeded to test these conclusions experimentally, not in the capillary viscometer, which, from this point of view, is theoretically useless, but in a modification of the concentric cylinder apparatus first used by Couette in 1890.

It has been mentioned before that the ideal arrangement of two parallel planes can be very closely approximated by using two concentric cylinders, the space between which is filled by the liquid to be examined, and this is the principle of Couette's apparatus. Fig. 2 shows a longitudinal section through the first apparatus I used; a second and improved type is before you. The outer cylinder D can be rotated at a uniform speed, while the inner one A is suspended from a wire B and carries mirror H, which allows the deflection to be read by telescope and scale in the usual way. The effects of the bottom of D and the liquid surface must be eliminated, which is done by the two guard cylinders F. When the outer cylinder rotates, the inner one is carried round by the viscous drag of the liquid until the torsion of the wire balances this drag. Theory shows that, when the end effects are completely eliminated, the deflection divided by the angular velocity is exactly proportional to the viscosity.

The sensitivity of the apparatus can be increased to any desired extent by using thin wires, and very low velocity gradients, which are of importance in these investigations, can be employed. We have gone down to an angular velocity of  $2.4^\circ$  per second, i.e. one revolution of the outer cylinder in 2.5 minutes.

(The apparatus was shown working with water at an angular velocity of about  $24^\circ$  per second, i.e. one revolution in 15 seconds.)

The first results on colloidal solutions with the apparatus were

published in 1913. Fig. 3 shows some of the viscosity curves of 0.5 per cent. gelatin solutions. The ordinates in this diagram are

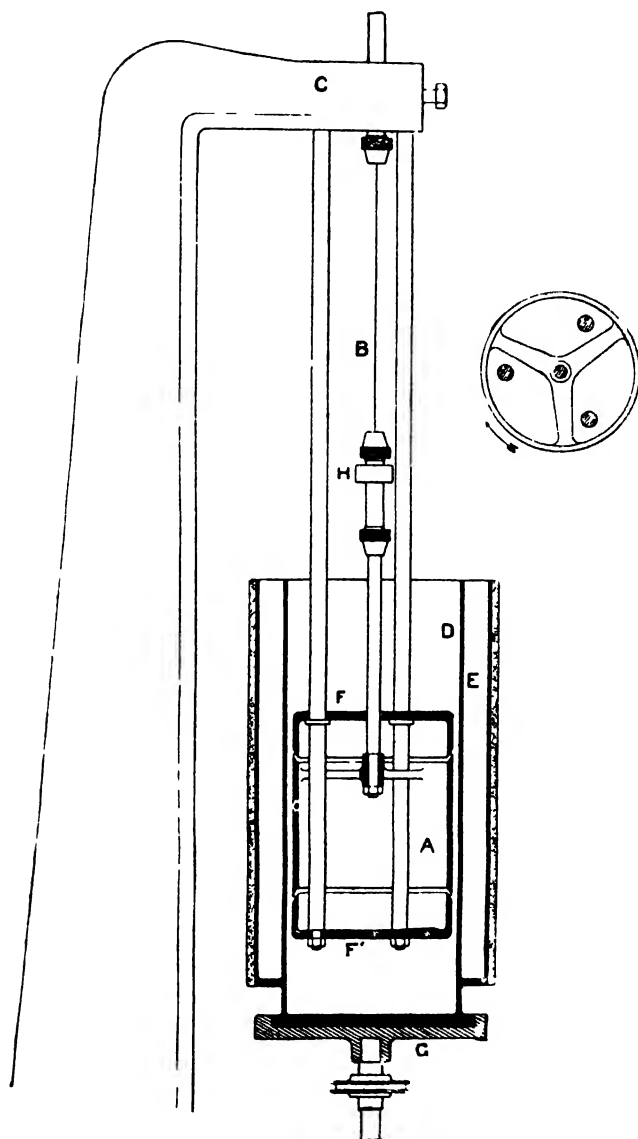


FIG. 2.

viscosities, the abscissæ angular velocities; the dotted line represents the viscosity of water, which is constant and therefore appears

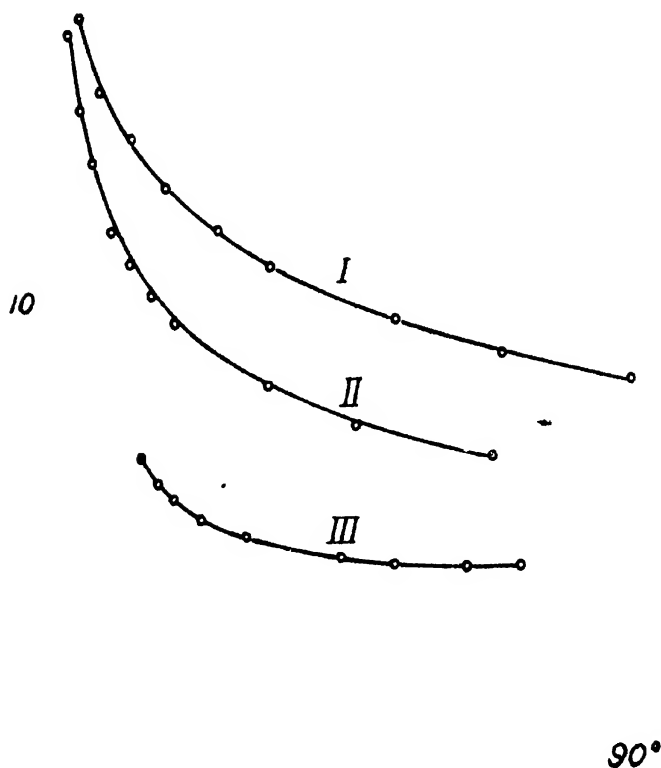


FIG. 3.

0.5% gelatin; I, 72 hours old; II, 48 hours old; III, 24 hours old.  
(Hatschek, 1913)

as a horizontal straight line. You will observe in the two upper curves that the viscosity at the lowest speed is about 2.5 times higher than at the highest speed, and that with increasing speed the

viscosity shows a marked tendency to become constant, i.e. the curves become horizontal.

Many other colloidal solutions have been studied in this apparatus both by us and by Professor Freundlich, who possesses a copy of mine, and has carried out numerous investigations with his pupils since 1923. It will be sufficient to show one more set of their results, obtained by Freundlich and Schalek (Fig. 4). Sodium stearate is a soap, and benzopurpurine and cotton yellow are two dyes, with quite different constitutions and many interesting physical properties. The curves are all of the same type, and also of the same type as those for gelatin shown in the previous slide. The viscosities at the lowest velocities are again two or three times higher than at the highest, and all of them give the distinct impression of growing asymptotically with increasing velocity.

A large number of substances of the most varied chemical character have been studied by other investigators, such as agar, gum arabic and starch, rubber in various solvents, nitro cotton in various solvents, etc. It may be said quite definitely now, that they all show the same behaviour, provided the range of velocity gradient used is sufficiently wide. One observer failed to detect any anomaly in the behaviour of gum arabic, and another in that of sodium oleate; by working at very low velocities we have however been able to show that these solutions behave like all the others, but the horizontal portion of the curve is reached at exceptionally low velocity gradients, and is therefore likely to be overlooked if this region is not examined.

Since this behaviour is thus characteristic of a very large number of colloidal solutions, and in the most striking contrast to that of normal liquids, it is of great importance to find some explanation of it. One which has been suggested by various authors, including Professor Freundlich, is that these solutions, unlike normal liquids, possess not only viscosity, but also rigidity. If this assumption is true, the liquid—to put the matter colloquially but picturesquely—will have to be stretched as well as sheared. It can be shown mathematically, by making the simplest assumption about this rigidity, that the result will be what has been found experimentally, viz. that the viscosity decreases with increasing shear.

The suggestion that solutions which nobody would hesitate to describe as liquids should yet possess one of the fundamental properties of solids is so surprising, that one is naturally anxious to have a direct demonstration rather than a mere inference from mathematical treatment. There is no difficulty in providing this demonstration with suitable apparatus—delicate and unsuitable for lecture experiments—which will be described later. I have, however, been fortunate enough to discover a solution which exhibits rigidity on such a scale that it can be demonstrated with extremely simple means in a most convincing manner. This liquid is a very dilute, about one-quarter per cent., solution of ammonium oleate, a soap

familiar to this Institution as material for soap bubbles. Its rigidity can at once be shown in this simple apparatus. A cylinder, weighted

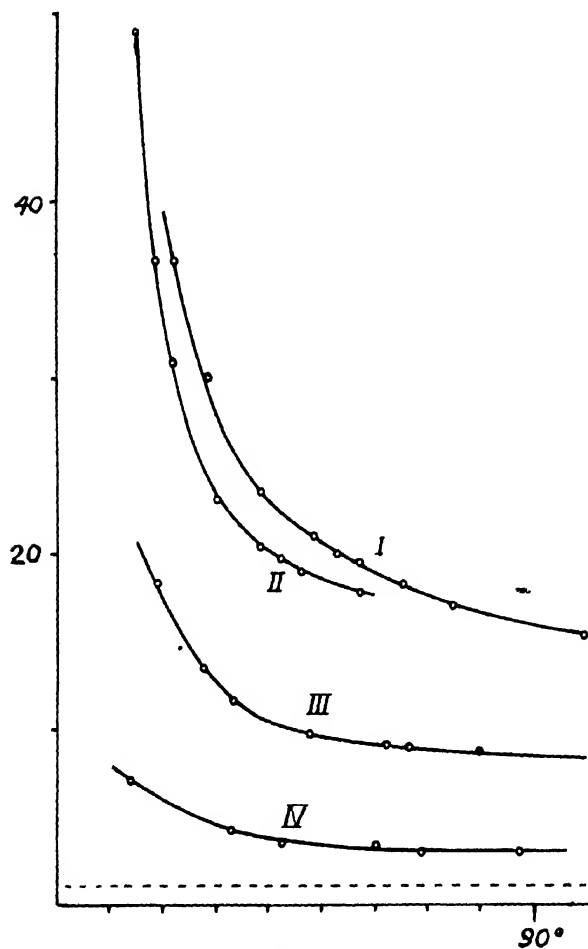


FIG. 4.

I, 0.42% cotton yellow; II, 1.0% cotton yellow; III, 0.1% sodium stearate; IV, 0.8% benzopurpurin.  
(Freundlich and Schalek, 1924.)

at the bottom and centred in a footstep, is suspended free in the solution (Fig. 5). If a spin is given to the cylinder it will, in a

normal liquid, revolve till the momentum is used up and then simply come to rest. The rigid ammonium oleate, however, behaves somewhat as would a hollow cylinder of rubber: the cylinder comes to rest, but is then pulled backwards.

The ammonium oleate solution is mechanically a very labile system, and its elastic properties depend very much on its treatment.

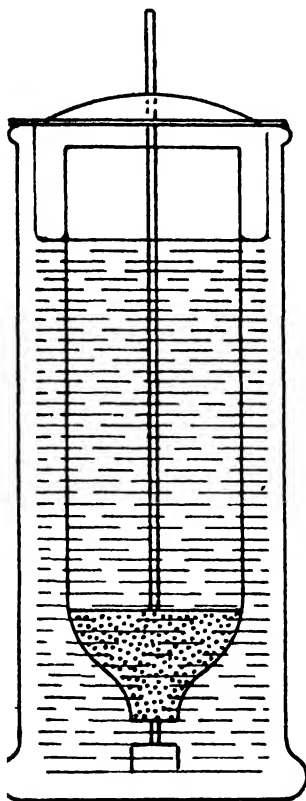


FIG. 5.

I understand they have given some trouble here in soap bubbles, and have been put down to impurities in the oleic acid. As other ammonium soaps which we have studied do not show the effect, this explanation does not seem adequate.

As the ammonium oleate exhibited such striking rigidity, it seemed to us an excellent means of testing the connection between rigidity and variable viscosity. We found that it exhibited another

striking anomaly, which can be described only by the statement, extravagant as it sounds, that the solution has no definite viscosity at all. It changes constantly, and as we have shown, periodically, during a long period of measurement.

This anomaly is fortunately unique. As regards rigidity, no other solution which has yet been examined shows this effect so strikingly, and to demonstrate rigidity, and especially to make actual measurements of the modulus, much more delicate means have to be employed. Schwedoff, in pursuing the line of investigation by Kundt, developed a method and constructed an elegant apparatus, with which he carried out—or at any rate published—a single determination, that of the modulus of a 0.5 per cent. gelatin solution, in 1889. About 18 years later, Rohloff and Shinjo, at Göttingen, investigated the rigidity of gelatin solutions by a different method, and over an extensive range of concentrations, ages and temperatures. We were anxious to obtain data on other substances besides gelatin, especially on those which had been used for viscosity measurements, and used Schwedoff's method.

The artifice of employing concentric cylinders, instead of parallel planes, is again employed, and the mathematical theory is formally similar to that of the Couette viscosity apparatus. A cylinder closed at the bottom is suspended coaxially in a cylindrical vessel containing the solution to be examined by a wire of known moment: in view of the smallness of the forces to be measured very thin and long wires have to be used, and the apparatus is excessively sensitive to vibration and changes of temperature. If the wire is twisted by a known amount while the cylinder is submerged in a normal liquid, the cylinder begins to follow it at once and continues to move until it has travelled through the same angle as the wire, i.e. until the torsion in the latter has disappeared. If, however, the liquid possesses rigidity and the wire is given a certain torsion  $\phi$ , the cylinder does not follow immediately, but only moves through a much smaller angle  $\omega$ , and stays in that position for some time, the rigidity of the solution now balancing the remaining torsion in the wire. From the angles  $\phi$  and  $\omega$  and the constants of the apparatus the modulus of rigidity of the liquid can be calculated.

A great difficulty in the use of the apparatus is the necessary high degree of sensitiveness. If a liquid possessing rigidity is simply poured into it, the wire deviates considerably from the zero position, and the strains in the liquid do not disappear for many hours or even days. Fortunately all the liquids examined lose their rigidity completely at or below 40°, and recover it on cooling; the usual procedure was therefore to charge them into the beaker hot and to begin measurements on the following day.

Table I shows a number of the moduli determined with the apparatus. These have to be expressed in milligrammes per sq. cm., while, as mentioned, the modulus of the gelatin jelly shown at the



beginning is of the order of grammes per sq. cm., and that of metals of the order of tons per sq. cm.

TABLE I.—MODULI OF RIGIDITY OF COLLOIDAL SOLUTIONS IN  
MGM. PER SQ. CM.

0.2 per cent.	gelatin, 24 hours old	.	.	.	0.87
0.5	" cotton yellow, 68 hours old	.	.	.	15.8
0.75	" " 20 "	.	.	.	18.9
0.75	" " 68 "	.	.	.	23.8
1.5	" mercury-sulphosalicylic acid, 20 hours old.	.	.	.	2.29
1.5	" " " 7 days old	.	.	.	3.24
1.5	" " " 23 "	.	.	.	18.9
0.3	" benzopurpurin, 20 hours old	.	.	.	0.75
1.0	" " 23 "	.	.	.	11.1
0.6	" ammonium oleate, 24 hours old	.	.	.	2.29

None of these solutions exhibit any rigidity at temperatures above 40° C.

It will be noticed that the ages of the solutions are given, and that the modulus increases with age. It has long been known that the viscosity of many colloidal solutions increases with age, and we have now demonstrated that the increase goes parallel with, and may be due to, an increase in rigidity.

Apart from this common feature, the solutions exhibit a great variety of behaviour. In some instances the presence of rigidity depends entirely on the method of preparation: thus solutions of benzopurpurine prepared cold show no rigidity whatever, only those prepared at about boiling-point. While all the solutions lose their rigidity on warming, their behaviour on cooling again varies: some are "rejuvenated," i.e. the effect of previous ageing is destroyed, while others on cooling still show their previous age.

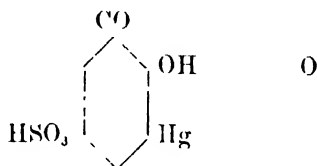
Since these solutions can support, unlike normal liquids, a small deformation, we should expect them to show accidental double refraction when they are disturbed, and as a matter of fact most of them do so, though in very varying degrees. The effect is shown well by cotton yellow in 0.2 per cent. solution. It is even more striking in mercury-sulphosalicylic acid in 1 per cent. concentration, as was first shown by Professor Wolfgang Ostwald, to whom I am indebted for the preparation. The effect is no doubt partly due to the presence of the mercury atom.

Since the solutions lose their rigidity one would expect them to lose the double refraction at the same time, and this is indeed the case. Heating is not feasible in the cells used here, but the mercury-sulphosalicylic acid also loses its rigidity and anomalous viscosity, and, at the same time, its double refraction, immediately on the addition of sodium or potassium chloride.

Although the solutions described show rigidity to a measurable degree, the properties of the liquid state yet manifest themselves, inasmuch as they do not, like elastic solids, support deformation for



much larger than molecules they are yet supposed to be modelled on the shape of the molecule, such as the long-chain molecules of the fatty acid salts, or the long chains of amino-acids which form proteins like gelatin. As mentioned, there is little or no direct evidence of such structures, and the extreme chemical and constitutional diversity of the substances whose solutions show anomalies makes the explanation improbable or inadequate. To mention one case only : ammonium oleate no doubt has a long-chain molecule, but the mercury-sulphosalicylic acid is a simple aromatic compound of the formula



which makes chain formation difficult to conceive.

It is, however, not only the extreme diversity of molecular structures which makes such attempts at explanation unconvincing, but we have experimental evidence showing beyond any doubt that variable viscosity can be produced simply by suspending in a normal liquid a small volume percentage of microscopic particles of nearly spherical shape. I showed in 1916 with Dr. Edith Humphrey that such suspensions (rice starch in an indifferent organic liquid of the same density) exhibited viscosities which varied with the velocity gradient exactly as do the viscosities of colloidal solutions. The measurements were repeated and extended last year, and Fig. 6 shows the viscosity-velocity gradient curve of 2, 4, 6 and 8 per cent. suspensions. These curves are in all particulars similar to those found with colloidal solutions; with decreasing velocity they appear to become asymptotic to the axis, while with increasing velocity they approach, and in the lower concentrations assume, a constant value.

There is no evidence, and certainly no probability, that these microscopic particles aggregate in any way into filaments or the like, and there is thus no possibility of ascribing the variable viscosity in this case to any special configuration or arrangement. Its cause must therefore be looked for in some effect which they produce on the surrounding liquid. There is a very large amount of evidence drawn from the most diverse phenomena to show that particles in a liquid are surrounded by layers in which the properties of the liquid are altered, so that the virtual volume of the particles is increased and that of the liquid reduced. The measurements on suspensions prove that these layers must extend further into the liquid than would appear from some other evidence, and that they must be labile enough to be affected by the shearing of the liquid. These considerations apply to all particles, whatever their shape or

arrangement, though the latter factors naturally add to the complications of the effect.

There is a further very strong argument for the view, that the cause of the anomalous viscosity of colloidal solutions has to be

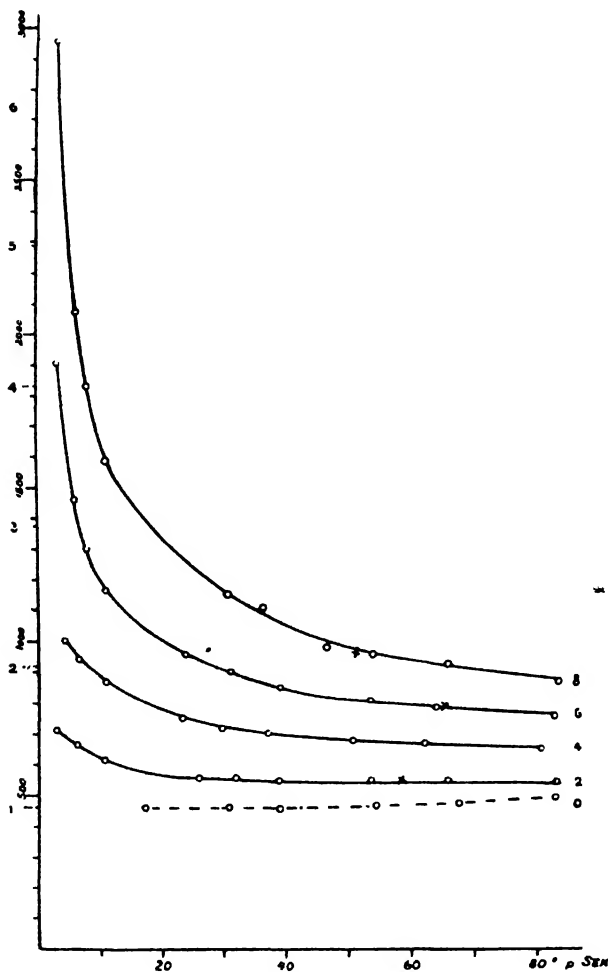


FIG. 6.

sought partly or largely in some change in the liquid, and that is the striking uniformity of their behaviour as regards temperature. Solutions of substances differing as widely as possible in their constitution behave alike, inasmuch as they lose their rigidity about the

same temperature, viz. 40°. It seems natural to look for the reason of this uniformity in the factor common to all the solutions, i.e. the water, for the properties of which this temperature is significant.

It would be tempting to speculate on the significance of the anomalies which have been discussed in regard to processes in organisms, all of which consist largely of colloidal material. I do not propose to do so, but to conclude by drawing attention to the general physical aspect of variable viscosity and rigidity in colloidal solutions. It is known that under enormous pressures solids behave like liquids, i.e. flow; colloidal solutions exhibit the converse behaviour: under exiguous stresses they approximate the behaviour of solids by exhibiting enormous viscosities. Many of them pass continuously into jellies, which, as shown at the beginning, behave within limits like elastic solids, and these steady transitions recall the maxim—which it is perhaps somewhat daring to recall in these days of quanta—that “*Natura non agit per saltum.*”

[E. H.]

Friday, January 20, 1928.

SIR ARTHUR KEITH, M.D. LL.D. F.R.S., Treasurer and  
Vice-President, in the Chair.

SIR WILLIAM BRAGG, K.B.E. D.Sc. F.R.S. M.R.I.,  
Fullerian Professor of Chemistry.

### Photo-electricity.

THE relations between light and electricity are of unending interest. More than fifty years ago the experiments of Faraday and the calculations of Maxwell culminated in the splendid electro-magnetic theory of light, on which subsequent research has built largely and firmly.

Even in the early days of the theory there was known to exist a peculiar and special relation to which the name of photo-electricity was given. The theory gave no ready explanation of it. Light falling upon a metal plate could cause the plate to become positively charged; ultra violet behaved better in this respect than visible light. When subsequently the electron was recognised and defined, it became clear that the photo-electric effect could be explained as due to an emission of electrons from the metal under the influence of the light, and various suggestions were offered as to the nature of the mechanism. It was clear that the absorption of energy from the electro-magnetic waves of light was replaced by the energy of electrons in motion; though at that time there was no obvious relation between the quantities of energy in the two forms. As time went on it was realised that this particular transformation was not an isolated effect; it was but an instance of one of the most important and widespread processes of physics. It was to be observed not only in the case of light but of X-rays and  $\gamma$ -rays also; and indeed in their case it was infinitely plainer and more accessible to experiment. But it also became continually clearer that the process was not to be explained in any simple fashion, if at all, by the original electro-magnetic theory of light, or by any natural development of that theory.

At the same time a number of other physical phenomena, and especially the relation between the quality of the radiation from a hot body, and the temperature of that body, showed also that the older theories were unable to account for the facts. They could be accounted for by supposing that heat could be radiated or absorbed only in parcels of definite size, no fractions being allowed. If such an idea might be reconciled with the undulatory theory, i.e., of

electromagnetic waves, at least it was not contained therein. This was the beginning of the quantum period.

In 1905 Einstein published a pioneer paper in the "*Annalen der Physik*" in which the quantum was given an identity even more definite than that which Planck had assigned to it in his studies on heat radiation. Light was to be regarded not as a uniform train of spherical waves but as a flight of "quanta," corpuscles of some form to be better known on closer acquaintance. By reverting to a corpuscular theory of light he was able to connect together the new facts, which were in such apparent discord with the undulatory theory. In doing so he, of course, shut his eyes for the moment to the marvellous and most successful development of the latter theory to the explanation of such phenomena as reflection, refraction and diffraction. He would simply find a new theory to connect together the new facts; this done, the new and old theories could be brought together in the hope of welding them together. As he announced in the title of his paper, he was going to take the heuristic point of view.

Since 1905 new discoveries of first-class importance have been made, but still there is no simple answer to the old question. The most recent and, so it is said, the most successful solution is given by the hypothesis of so-called Wave-Mechanics, due largely to M. L. de Broglie and Dr. E. Schrödinger. It is now the subject of eager discussion in mathematical and physical circles.

The Managers of the Royal Institution have invited Dr. Schrödinger to give a short course of lectures on Wave-Mechanics at the Royal Institution, and have been gratified by the acceptance of their invitation. It has been arranged that the lectures shall be given on March 5th, 7th, 12th and 14th, at 5.15 p.m. Also Professor Whittaker, of Edinburgh, has accepted an invitation to give the Friday Evening Discourse on March 16th, on which occasion he will try to summarise for the benefit of our Members the features of the new position.

My discourse this evening is meant to be of a preparatory nature. I would like to set out the observed facts for which it is so difficult to find a common explanation, so far as it is possible to do so in the short time at my disposal. I cannot, of course, tell the whole story; I can only describe a few of the most important details of it.

Einstein begins his 1905 paper by pointing out, as a curious fact, that matter is now looked on as a collection of discrete particles, while light, which resembles matter in being one of the great phenomena, is treated as a continuous distribution in the space over which it passes; and he suggests that it would be well to consider a discrete view of light also. He then enumerates certain experimental results which would be in obvious agreement with the new theory, though not with the old. Most of them are beyond our capacity to consider in the short hour of this discourse; but two of them may

well be considered by us as amply sufficient to illustrate our argument and easily demonstrable even on the lecture table.

The first of them is summed up in what is called Stokes's Law of fluorescence. When light falls upon a fluorescent substance the fluorescent light evoked is always of longer wave-lengths than the exciting light; in other words, its frequency is less. Now, if a corpuscular theory of light is to be adopted, wave motion of a given frequency must be replaced by some characteristic of the corpuscle; and it appears that the two, and only two, characteristics of a wave-motion, namely, frequency and intensity, are to be replaced respectively by individual energy and numbers of corpuscles. This has to be done in order to explain both the results we are considering and a number that we are not. On the corpuscular theory a beam of violet light is a flight of corpuscles each having a certain energy which is proportional to the frequency of the light. A beam of green light is a flight of corpuscles each having a certain energy less than the other, because the frequency is less. It is easy to imagine that the flight of more energetic corpuscles may be degenerated by impact with the body into a flight of less energetic corpuscles. But it is very difficult to see how undulations of one wave length can on meeting material substances be converted into undulations of a different wave-length.

A still more striking argument is found in the photo-electric effect itself. Lenard had shown three years before that when the electrons came out of the solid body under the influence of the light their individual energy did not depend upon the intensity of the light, but on its frequency; the intensity affected only their number. This was an extraordinary result. It might have been thought that the more energetic or violent the waves of light which caused the emission of electrons, the greater the velocity with which the electrons would start on their way. And as to the influence of frequency, it would be difficult to say how it would go; though one would not readily expect it to be the sole arbiter of the velocity. But if light was corpuscular the process, though still unexplained in detail, ceased to look so strange. Each corpuscle acting independently would cause the emission of an electron. The intensity of the beam of light would depend on the number of corpuscles it contained, and their impact on the body would cause a proportionately large emission of electrons, making the photo-electric effect. And light of high frequency would on the corpuscular view consist of swiftly moving corpuscles which, having large energy, would cause the emission of relatively swift electrons. The whole phenomenon, by its character and definiteness, spoke entirely for the corpuscular theory. Einstein explains the point perfectly clearly in his famous paper of 1905, and suggests that, if he is right, far more careful quantitative observations would be justified, as they would give an authoritative verdict on the validity of the theory which he proposed. He suggests that



workers might bear his views in mind when proceeding with their experiments.

Einstein's theory must have been discussed exhaustively; but, so far as I know, no allusion to it, or criticism, is to be found in the principal journals of physics for some years afterwards. In fact, it was not until seven years later that Richardson and K. T. Compton carried out the careful measurements which Einstein suggested.

The results were in absolute accordance with the exact rules which he had supposed would govern the photo-electric effect, having based them on the less well-defined information which was available when he first wrote.

I must now be permitted to describe some experiments which I carried out in Australia twenty years ago, in conjunction with several helpers, in particular R. Kleeman and J. P. V. Madsen. I had been working out certain laws which governed the passage through matter of the X-rays emitted by radium; and I had tried to carry over the information so obtained to an investigation of the behaviour of the  $\beta$  and  $\gamma$ -rays. Now when  $\gamma$ -rays fall upon a substance they excite  $\beta$ -rays, which are electrons in very swift motion. In fact the analogy with the photo-electric effect is exact; for the rays as we now know are a form of light of very high frequency. The characteristic features of the photo-electric effect appear here also and greatly emphasised. The swift  $\beta$ -rays are far easier to detect and to examine than the electrons set in motion by light. The parallelism was not then so obvious as it is now, and for my own part I could not then believe in its existence. Our experiments fitted in perfectly with a corpuscular hypothesis of the nature of the  $\gamma$ -rays; and I supposed that the undulatory theory of light was unshakable. I should, of course, have thought otherwise if I had been aware of Einstein's paper, to which I have already referred; but it is easy to miss a single reference when one is in a very isolated laboratory, and, as I said before, there are few if any allusions to the paper in the current literature of the years immediately following its appearance.

Our experiments in 1907 and 1908, coupled with others to which we were able to refer, led us to the following conclusions:—

- (1) When  $\beta$ -rays or  $\gamma$ -rays were incident on matter the energy of any resulting secondary radiations of any kind,  $\beta$  or  $\gamma$ , came from the rays. There was no "induced" radioactivity; no case of the energy of an atom being tapped. The adoption of this hypothesis simplified all further considerations of the phenomena.
- (2) The so-called hard or very penetrating  $\gamma$ -rays produced swift and penetrating  $\beta$ -rays; soft  $\gamma$ -rays produced slow  $\beta$ -rays.
- (3) The penetrating power or quality of the  $\beta$ -rays, produced by the action of  $\gamma$ -rays, depended only on the quality of the  $\gamma$ -rays, not upon the intensity of the  $\gamma$ -rays nor

upon the nature of the substance in which the transformation of energy took place; it was practically the same as that of the  $\beta$ -rays issuing from the radium itself.

- (4) The  $\beta$ -rays produced in any substance by the action of the  $\gamma$ -rays moved at the outset in the original direction of the  $\gamma$ -radiation.

The last statement is capable of simple demonstration in the lecture room. The necessary apparatus is shown in the figure, which is taken from a paper by Madsen and myself. The radium is buried in a mass of lead, at the foot of a conical pit. Both  $\beta$ - and  $\gamma$ -rays issue from the mouth of the cone, but the former are turned aside by a strong magnet. The  $\gamma$ -rays pass on alone into an ionisation chamber. The beam of  $\gamma$  rays is not quite free of  $\beta$ -rays because the latter are aroused even in the air through which the  $\gamma$ -rays pass on their way to the chamber, but the magnet has removed most of them. If now a carbon plate be placed in the path of the  $\gamma$ -rays as they enter the chamber there is a large increase in the ionisation current; the  $\gamma$ -rays as they pass through the block on their way generate  $\beta$ -rays, which cause the observed effect. But if the carbon plate be placed on the far side of the chamber so that the  $\gamma$ -rays strike it on the way out, there is a relatively small increase in the current. Yet the rays must have generated  $\beta$ -rays to very nearly the same amount in both positions of the plate; and the dissymmetry between the intensities of the "emergence and incidence"  $\beta$  rays (the one is ten times that of the other) tells us that the  $\beta$ -rays are largely thrown forward as they are produced. In fact, from what is otherwise known of the behaviour of  $\beta$ -rays on their way through matter, we might suppose that the  $\beta$ -rays were thrown forward exactly in the line of the  $\gamma$ -rays, for the substance of the carbon screen would turn back a certain proportion of the rays, and the incidence radiation could be accounted for in this way. Nevertheless, we know now, from more accurate work which we shall presently consider, the  $\beta$ -rays are not so closely tied down to the forward movement, and when the  $\gamma$ -rays are soft and the  $\beta$ -rays relatively slow the difference between emergence and incidence is less marked. The experimental difference is also much less when the carbon plate is replaced by screens of higher atomic weight.

Thus again we have those characteristics which led Einstein to suggest a corpuscular theory of light in order to account for them when manifested in the photo-electric effect. Here they are displayed in an immensely enhanced degree. Consider the  $\gamma$ -ray as a spherical wave weakening as it spreads away from its source. It arrives at a certain atom; a  $\beta$ -ray springs out of the atom with an energy which is just the same, no matter how intense are the  $\gamma$ -rays, or how the intensity has faded with distance. Moreover, it possesses

a forward momentum which could not possibly, by millions of times, be given to it by the wave, although a wave can impart a certain momentum to an encountered obstacle.

These questions of energy and momentum are even more obviously displayed in the case of the X-rays and the electrons which are concerned both in their production and their absorption. In the X-ray bulb the electron is driven with a certain speed against the anticathode, the X-ray which is thereby excited passes away and, falling on some substance, it may be far or near, sets in motion an electron which has a speed comparable with, sometimes nearly equal to, that of the original. Here again is the same kind of transformation of energy, which is simply pictured as carried, unchanging on its way, either by the  $\beta$  electron or the corpuscle of the  $\gamma$ -ray.

I may say, I think, that in these experiments we were, though unwittingly, carrying out Einstein's suggestion that the corpuscular hypothesis deserved careful exploration; and the results were in entire agreement with his hypothesis. It was true, however, that I thought of the X-ray and  $\gamma$ -ray problems as distinct from that of light; and I ventured prematurely to give form to the corpuscle as a neutron, an electron compensated as to its charge by the addition of a neutralising amount of positive.

In 1910 and 1911 C. T. R. Wilson published accounts of his experiments with his fog chamber. These rendered obvious to the eye those tracks of the various rays through a gas which we had endeavoured to map out by more indirect means, and entirely confirmed the conclusions that had been reached. I may perhaps be allowed to illustrate this in the special case of the  $\alpha$ -rays, though they do not fall within the limits of our subject. In Fig. 1 is shown a set of tracks of  $\alpha$ -rays drawn so as to be in accord in the first place with the work done in Adelaide; and also to agree with the more recent experiments on their scattering performed by Rutherford and Geiger. Fig. 2 is from a photograph of one of the well known early achievements of Wilson. It may be a matter of interest that on a certain occasion in the Cavendish Laboratory at Cambridge we showed them to each other for the first time.

Wilson's photographs of the tracks of X-rays,  $\beta$ -rays, and cathode rays, placed the argument on a different plane; and their beautiful detail opened up the way to quantitative measurements which had seemed impossible. It was now obvious to the eye that X-rays and  $\gamma$ -rays did not of themselves ionise a gas, but set in motion electrons which did so. The lengths of the tracks of these electrons in a gas could be measured, and their initial velocities be calculated therefrom; their directions of ejection could also be observed. All fitted in perfectly with the quantum theory of the X- and  $\gamma$ -rays, even when refinements could now be studied, as, for example, the differences in velocities of ejection which were to be expected on Bohr's theory of stationary state.

In 1913 the discovery of the diffraction of X-rays by the crystal opened up a new point of view, and once more changed, or rather enlarged, the aspect of the question. It now appeared that X-rays and  $\gamma$ -rays in these effects behaved like long trains of spreading waves, and no clear picture of what happened could be obtained in any other way. In this matter the corpuscular theory was at sea. Even the old single pulse theory was in no better case, because it did not provide the regular succession of similar waves which was required to account for the crystal effect. The new discovery con-

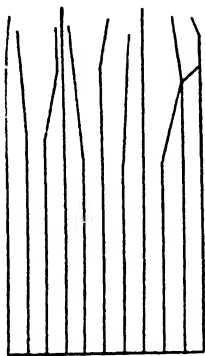


FIG. 1.

Suggested forms of the paths of a particles projected upwards from radium at R R.

(From "Studies in Radioactivity,"  
by Sir W. H. Bragg  
Courtesy of Macmillan & Co, Ltd)



FIG. 2.

From photograph of  $\alpha$ -ray tracks  
by C T R Wilson

solidated the position, linking together light, X-rays and  $\gamma$ -rays as one phenomenon; if they were regarded from the point of view of the undulatory theory they were all waves which differed only in frequency. If any other point of view was taken, that of a corpuscular theory for example, the equivalence must be expressed in some equally effective fashion. On the other hand, the simplification emphasized the difficulties of the position, since it left no escape from the necessity of finding a theory which could with equal ease and effectiveness express itself in terms either of waves or of

corpuscular projectiles. Whether or no this has yet been done by any of the theories now in being is indeed the question of the day; our judgment will, I hope, be assisted by the lectures that are to follow.

Meanwhile matters have by no means remained stationary since the powers of X-ray and crystal analysis have been put into our hands. With the aid of the X-ray spectrometer we can measure with extreme accuracy the wave-lengths and frequencies of X-rays. When X-rays are incident upon a substance they are to some extent scattered as such, just as a ray of light is scattered in passing through a dusty atmosphere. This is apart from the photo-electric effect, namely the production of swift moving electrons at the expense of the energy of part of some of the incident rays. The X-rays are scattered by the atoms and electrons, the light being of coarser wave-lengths is scattered by the coarser particles of dust. Now when  $\gamma$ -rays, which are very fine X-rays, are scattered it has been often remarked that the scattered rays are somewhat softer than the originals. A. H. Compton used the spectrometer to examine if possible this softening, if X-rays could show it. They not only did so, but the experiments showed a real change of wave-length varying according to circumstances, and obeying simple rules. It appeared, in fact, that there was a definite small change in wave-length, which depended on the angle of scattering, but not on the original wave-length nor on the nature of the scattering material. Figs. 3 and 4, taken from Compton's new book "X-Rays and Electrons," show the effect very clearly. They represent the results of the spectrometer observations; in each curve one hump is due to rays that have not been altered by scattering, and have preserved the same frequency as the original beam. A second hump is the evidence of the "modified" scattering; the relative amounts of the two vary with the scattering substance. Every material returns something of both kinds; but the lighter the atom the more intense is the modified in comparison with the unmodified; at the same time, as already said, the change of wave-length is constant from substance to substance. The phenomenon is a little like that of fluorescence, but the likeness is only on the surface. But this is true of both, that the undulatory theory does not suggest a simple explanation in either case. I ought to say that Professor Raman, of Calcutta, has just announced in "Nature" that he is able to explain the Compton effect on classical lines, and promises to give his new theory in full.

On the other hand, the corpuscular theory gives at once an explanation which is relatively simple, and allows quantitative deductions to be made which are in entire agreement with the facts. If a corpuscle or "photon," to use the term which has lately been

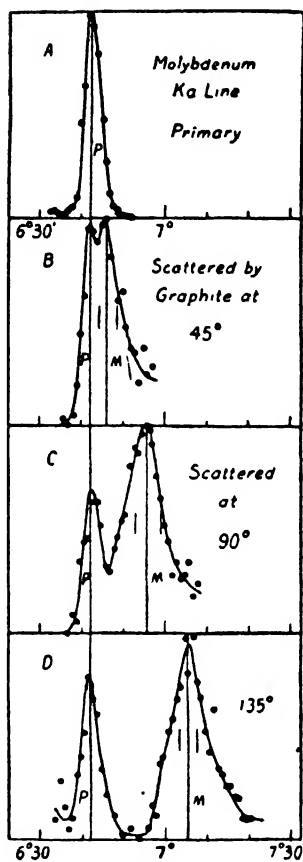


FIG. 3.

(Courtesy of D. Van Nostrand  
Company, Inc.)

Ascissæ represent angle of scattering and ordinates representing intensity. The hump on the left of each figure represents the intensity of the scattered radiation, which has the same wave-length as the primary beam. The hump on the right marked M represents the intensity of the modified portion of the scattered radiation.

This figure shows how the effect depends on the angle of scattering.

suggested, comes into collision with an electron, as it can do in traversing any material, it is possible to work out the consequences as if for an impact between two billiard balls, assuming only that photon and electron have both of them momentum and energy, the quantities being reckoned according to rules already established. The result is that the photon goes off with somewhat diminished energy; it has lost "frequency," and the calculated loss is exactly that which is shown in Fig. 3 as the result of experiment. Moreover, the electron ought to start off with a certain amount of energy, and when Wilson's photographs are examined the predicted tracks are found on them. Thus the spectrometer, which is based on an undulatory theory of X-rays, has established facts which are in accord with the corpuscular theory.

When we see in this way that radiation, which has always been thought of as undulatory, can on occasion display corpuscular properties, we are prompted to ask whether moving electrons —  $\beta$ -rays, cathode rays, and so on — which we have always considered as corpuscular, may not behave sometimes like waves? The answer appears to be in the affirmative. In America Davisson and Germor have recently described most remarkable experiments in which moving electrons are reflected by crystals in a manner bearing an obvious, though diffuse, resemblance to the now well-known reflection of X-rays, and the latter is always explained on the basis of an undulatory theory. More recently still, Prof. G. P. Thomson, of Aberdeen University, has shown that when electrons are shot through a very thin film of metal, haloes are formed upon a

photographic plate on the other side of the metal, which may be explained qualitatively and quantitatively if the electrons act as waves in passing through the minute crystalline particles of the metal film. Prof. Thomson has promised, I am glad to say, to give us an account of this work in a Friday Evening Discourse

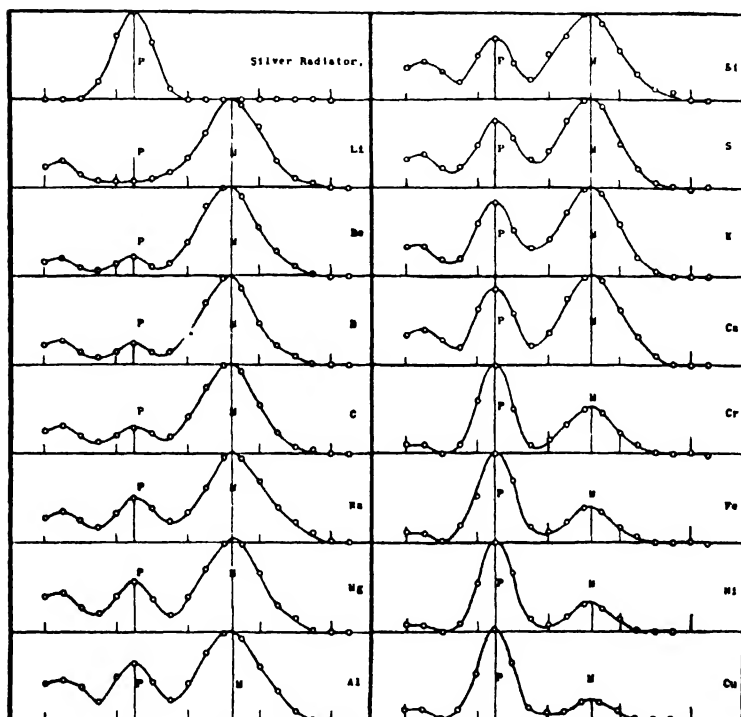


FIG. 4.

(Courtesy of D. Van Nostrand Company, Inc.)

In Fig. 2 the scattering substance is modified, and it is to be observed that the less the atomic weight of this substance the greater is the relative magnitude of the modified portion.

after Easter, and this will follow naturally on the lectures by Dr. Schrödinger and Prof. Whittaker.

I hope that this brief sketch of the present position will give some ideas of its extraordinary and fascinating difficulties. Perhaps the details of the picture are sorting themselves out, and we shall see before long where we have failed to see some important point which

was required for the complete resolution. When the picture is finally clear there will no doubt be atoms in it, electrons, wave motions, energies, momenta, and so on. But have we got them all rightly joined up? Perhaps wave motion belongs to more than the photon, or to something else than the photon? We can only wait.

[W. H. B.]



Friday, February 3, 1928.

SIR ALMROTH E. WRIGHT, K.B.E. C.B. M.D. LL.D. F.R.S.,  
Vice-President, in the Chair.

E. C. C. BALY, C.B.E. F.R.S.,  
Professor of Inorganic Chemistry, University of Liverpool

### Photosynthesis.

THERE is no process within the confines of Chemistry which is of greater interest and importance than that by means of which the living plant prepares the food on which its life and growth depend. This food consists of starch and sugars, together grouped under the general name of carbohydrates, and of certain nitrogen-containing compounds known as proteins. The material from which the plant starts is carbonic acid, or a solution of carbon dioxide, which it obtains from the air, in water which it obtains through its roots from the soil. From this substance alone the plant is able to prepare its supply of carbohydrates, and it is true to say that this chemical process is the fundamental basis of the whole of terrestrial life. This may truly be asserted because the production of the proteins is very closely associated with it and the initial stage is common to the two.

The formation of carbohydrates from carbonic acid when expressed by a chemical equation looks simple enough. There is no doubt that the first product of the process that can be recognised in the plant is a simple sugar, and thus the equation can be written



where the simple carbohydrate is either glucose or fructose. These simple sugars undergo condensation immediately they are formed to give cane sugar or one of the starches, and these changes can readily be written as simple chemical equations.

The mechanism by means of which the plant achieves the synthesis of these complex compounds from carbonic acid has long been a mystery to chemists and to botanists. It is known that the agency used by the plant to effect its purpose is sunlight, and thus the term photosynthesis has been applied to the operation. It is also known that the plant makes use of certain pigments, such as chlorophyll, and it is to these that the colour of the leaves is due. The mystery

of it all lay in the fact that no one knew what actually takes place, and, indeed, the more chemists and botanists explored, the more puzzling did the problem seem to be.

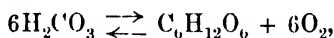
Perhaps the most puzzling fact of all is that the plant only makes use of sunlight, when all our previous knowledge of light reactions leads us to believe that such light is quite incapable of inducing photosynthesis. This may readily be understood if the amount of energy involved in the synthesis is considered. It has been proved experimentally that in order to synthesise one gram molecule (180 grams) of glucose or fructose there must be supplied to the carbonic acid a minimum quantity of energy equal to 673,800 calories. Whilst it is known that the plant manages in some way to absorb the necessary energy in the form of light, the physicist tells us that it cannot directly absorb enough energy from sunlight. Thus the photosynthesis can be brought about by red light of the wave-length  $660\mu$  when the energy directly absorbed can only be 260,000 calories, which is far below the minimum quantity required.

The experience gained from the ordinary reactions of photochemistry leads to the belief that if it is required to convert carbonic acid into sugars by means of light alone, it will be necessary to use ultra-violet light which is absorbed by carbonic acid, that is to say, light of wave-length  $210\mu$ . It is obvious from this that some unknown factor is operating in vital photosynthesis.

In any endeavour to elucidate the mystery, it is evident that the first line of enquiry must be to study the action of the short wave ultra-violet light upon carbonic acid. This was first investigated by Moore and Webster in 1913, who found no evidence of any reaction taking place. They found, however, that in the presence of certain catalysts, such as colloidal iron hydroxide, small quantities of formaldehyde were produced. Since these results appeared to be at variance with general experience in photochemical investigations, they were again examined some years later in Liverpool, and it was then found that when a stream of carbon dioxide was passed through water irradiated by the light from a quartz mercury lamp, small quantities of formaldehyde were produced. This result seemed to be very satisfactory, since the formaldehyde could be looked upon as an intermediate stage on the way to carbohydrates, especially in view of the fact that Moore and Webster had proved that formaldehyde was converted by light into substance, with properties similar to the simple sugars.

Our observations were criticised by Porter and Ramsperger, who stated that if rigid precautions were taken to guard against the presence of every trace of impurity, no formaldehyde was produced. The suggestion was implied by them that the origin of the formaldehyde was to be found in some unknown impurity. There is, however, an alternative possibility, and one which is more in keeping with the known facts of the natural photosynthesis in the living leaf. There

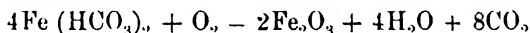
is no doubt that in this reaction the carbonic acid is converted directly into carbohydrates and that formaldehyde as such is not produced, and it seemed that the most probable explanation of the discrepancy between our results and those of Porter and Ramsperger was that the action of the ultra-violet light is to establish a photochemical equilibrium.



which reverts to carbonic acid again in the dark. In the presence of oxidisable impurities a small amount of carbohydrates will be formed, which will be photochemically decomposed to formaldehyde. This decomposition of all the carbohydrates by means of ultra-violet light is well known.

There is no need to give here the details of the experiments which were carried out to test this view, and it is sufficient to say that conclusive proof was obtained of the reality of the equilibrium: that is to say, carbohydrates were found to be present in the solution during irradiation by ultra-violet light, and these vanished very quickly after the irradiation was stopped.

This gave us at once a starting point, because it seems evident that if a harmless inorganic reducing agent were added to the solution, carbohydrates should be formed in quantity on exposure to the ultra-violet light. Such a reducing agent is ferrous bicarbonate, and great hopes were raised when it was found that a saturated solution of this compound, which was completely colourless when prepared, gave a copious precipitate of ferric oxide on exposure to ultra-violet light. It was evident that the oxidation took place by reason of the oxygen in the carbohydrate equilibrium in accordance with the equation



and indeed it was found that on evaporation of the exposed solution a simple sugar was obtained. The quantity produced was very disappointing and far less than was anticipated, and the conclusion was forced upon us that some unknown factor was taking part in the process.

During many unsuccessful endeavours to improve the yield of the carbohydrates, it was noticed that the ferric oxide was not produced in the body of the solution, but only on the walls of the quartz containing vessels and on the surface of the iron rods used to make the bicarbonate. This led us to suspect that the surface was a determining factor, and we at once changed the experimental method so as to increase the surface as much as possible. In order to secure this a suspension of pure aluminium powder in water, maintained by a stream of carbon dioxide, was exposed to ultra-violet light. Increased yields of carbohydrates were at once obtained, but it was also found

that the best yields were obtained when the aluminium powder had been allowed to coat itself with hydroxide by remaining in contact with the water before the exposure to light. This latter observation very materially changed our ideas, since it established the fact that the surface phenomenon is of far greater importance than the reducing action, and indeed raised the question as to whether the latter plays any rôle at all in the process.

In order finally to decide this question an aqueous suspension of pure and freshly prepared aluminium hydroxide, maintained by a stream of carbon dioxide, was exposed to ultra-violet light. There was obtained after filtration and evaporation of the solution a quantity of carbohydrates equal in weight to that produced when aluminium powder was used. This conclusively proved the fundamental significance of the rôle played by the surface, and at the same time the reducing action was found to be entirely unnecessary. Identical results were obtained with other powders, such as aluminium, zinc, and magnesium carbonates.

During the course of these experiments it occurred to one of my students (Dr. W. E. Stephen) that if a green powder were used in place of the white ones the photosynthesis might take place in visible light, the green colour being suggested by the green colour of the plant-pigment chlorophyll. This was found actually to be the case, since a suspension of nickel carbonate maintained by a stream of carbon dioxide in water, on exposure to the light from an ordinary tungsten filament lamp, gave a larger yield of carbohydrates than any of the white powders in ultra-violet light. We soon found that there was no especial virtue in the green colour, and that equally good results were given by pink cobalt carbonate.

Apart from the interest which accrues from the fact that the photosynthesis is thus achieved in a way which shows a real analogy with the natural phenomenon, the method with a coloured surface and visible light has the very material advantage in that the danger of photo-chemical decomposition by ultra-violet light is completely eliminated, with the result that the products are obtained in a purer state.

From the above description of the direct photosynthesis of carbohydrates from carbonic acid in the laboratory several points arise which require discussion and explanation. In the first place it may be stated that the most rigid control experiments which we could devise have definitely established the fact that the carbohydrates are not due to the presence of impurities.

One of the greatest difficulties met with in this work was the preparation of the various materials used for the surfaces, since it is absolutely essential that these be completely free from any trace of alkali. It is well known that when metallic hydroxides and carbonates are precipitated they tend to absorb the alkali, and the removal of this is extraordinarily troublesome. The absence of any alkaline

reaction in the filtrate after the powder has been boiled with water is no criterion of purity, and the only satisfactory method is to pass carbon dioxide into a suspension of the powder in water for two hours in the dark, and the filtrate after concentration must yield no weighable quantity of alkaline carbonate.

It was frequently found that the carbonates of nickel and cobalt, even when completely freed from alkali, were entirely ineffective in promoting photosynthesis. These can, however, be activated either by heating to  $120^{\circ}$  or by exposure in thin layers to ultra-violet light, and this fact afforded a very convincing method of carrying out controls. A quantity of one of these inactive powders gives no trace of carbohydrates when exposed to visible light in the manner described. The same sample of powder when activated and used in the same apparatus, with the same water, the same light, and carbon dioxide from the same source, gives a good yield of carbohydrates. So, once and for all, is all doubt removed as to the possible effect of impurities.

For the benefit of those who may wish to repeat these experiments, it may be stated that more recently it has been found possible to prepare nickel carbonate by a new method which is free from the objections characteristic of its precipitation by means of alkali carbonate. A solution of carbonic acid in conductivity water is electrolysed, the electrodes being made of nickel plates. The current is taken from a 220 volt circuit, and sufficient resistance is intercalated to reduce the current density to from 1 or 2 ampères per sq. dcm. The electrolyte is cooled by glass coils through which a stream of water is maintained. With electrodes 190 sq. cm. in area it is possible to prepare 30 grms. of pure carbonate in 24 hours. The carbonate should be collected every day by filtration, and it is advisable to clean the electrodes with emery paper every third day.

To sum up the results, so far as they have been described, it has been found possible in the laboratory to produce carbohydrates directly from carbonic acid by a process which is physically similar to that of the living plant. The essential difficulty in our understanding of the natural photosynthesis has been solved, namely the use of visible light as the agent in a process which the elementary laws of photochemistry taught us to believe could only be achieved by means of ultra-violet light. As so often happens the explanation when found is very simple. The great amount of energy required to convert the carbonic acid into carbohydrates is supplied to it in two portions, one by the surface and the other by the visible light.

Nothing has as yet been said of the actual carbohydrates which have been photosynthesised in the laboratory. Although as yet our information is still meagre, there is no doubt that the photosynthetic syrup is a mixture containing glucose or fructose, or both. There are also present more complex carbohydrates, which can be resolved to the simple sugars by the action of dilute acid. The

analogy with the products of natural photosynthesis is too close to be passed by without comment.

Although it has not as yet been possible to carry out a complete analysis of this syrup, owing to the difficulty of preparing a sufficiently large amount, interesting information has been gained from the investigation of the sugar syrup obtained by the action of light upon formaldehyde solution. This has been pursued during the last three years. We owe a debt of gratitude to Sir James Irvine for the signal help he has given us in this work. He himself was the first, in association with Dr. Francis, to prove that glucose is one of the substances actually produced. By oxidation of the sugars to the acids by means of bromine, and the crystallisation of the salts of these with brucine, cinchonine and quinine, we have obtained d-gluconic and also d-erythronic acids. This not only confirms Irvine and Francis in their proof of glucose, but it also proves that fructose is formed just as in the living plant. In addition to that, there is produced a mixture of complex acids which afford convincing evidence of the synthesis of complex carbohydrates.

Although it may be thought that the use of formaldehyde as the starting point takes away something from the interest, yet it must be remembered that it makes but little difference whether in actual fact we start from carbonic acid or formaldehyde. Without doubt the first substance, transiently formed in either case, is the same, namely activated formaldehyde which polymerises to the sugars.

The similarity between the vital and the laboratory processes is not confined to the fact that the products from the two are the same. Botanists tell us that in the living plant the photosynthesis takes place on a surface, so also is a surface necessary in the laboratory. It has been found possible to compare the quantities of carbohydrates synthesised for equal areas exposed to light in the case of living leaves and the glass vessels of the laboratory. These quantities are about the same. Some plants produce more and others produce less than we are able to synthesise. This similarity may be emphasised, because surely Dame Nature in the living leaf has produced the best machine she could for her purpose of food production for her children of the vegetable kingdom.

There is yet another striking feature which is common to the two, photosynthesis *in vivo* and *in vitro*. The light must not be too strong in either, for if it is too strong then harmful results at once supervene. This is due to the poisoning of the surface by the oxygen which is set free. In both cases this poisoning slowly rights itself, and in both the synthesis must not proceed at a greater rate than that of the recovery of the surface from its poisoning.

In fine, so far as we have been able to carry the investigations, the processes in the living plant and in the laboratory show most striking resemblance, not only in the compounds which are formed, but in every feature which is characteristic of either of them.

For my own part I would go further than this, because I believe that these experimental results help us to gain some understanding of the chemistry of life, the chemistry which is so different from that of man's achievements with his test tube, flask and beaker. Within the confines of vital chemistry reactions take place which are so far outside our own experimental experience that it came to be believed by many that they were under the control of a mysterious force, to which the name of *vis vitalis* was given. One of these processes has come within our purview to-night, the condensation of the simple sugars, glucose and fructose, to form cane sugar, starch and inulin. No one has yet succeeded in effecting these syntheses in his laboratory, but it would seem that something of that nature takes place in our photosynthesis. Why then is it that even this step forward has been gained?

The one lesson that we have gained from photosynthesis is, that the definitive factor is the very large amount of energy which must be supplied to the carbonic acid before the synthesis of the simple sugars takes place. The means of supplying that energy do not concern the argument. The synthesis proceeds at an energy level which is far higher than is the case in the reactions of ordinary chemistry, and the sugars are formed at that high energy level. I myself believe that the condensation reactions to give the more complex carbohydrates are those which are characteristic of the simple sugars when they exist at the high energy level. The reason why no one has succeeded up till now in inducing these reactions to take place is because no one has hitherto been able to supply the large energy increment necessary.

I myself believe that we find in this the key which unlocks the door of vital chemistry, and that the chemistry of all life is one of high energy, our laboratory experience being confined to the chemistry of low energy. From this view point I see a wondrous vista unfold itself, wherein new understanding, new hopes and new possibilities reveal themselves. Health and vitality must essentially depend on the high energy level being maintained; any lowering of that level will lead to poor health and weak vitality. Knowledge comes to us of the means whereby the high level may be kept unimpaired. The most important sources from which we can absorb high energy are fresh food and ultra-violet light. From the one we learn the necessity of the rapid distribution of our food supply before its high energy is lost, from the other we gain a real understanding of the benefits of ultra-violet light therapy, and, more important still, of the dangers of its misuse. We gain an insight into the chemistry of vitamins, which in the light of our new knowledge reveal themselves as stores of high energy, bottled sunshine so to speak, which yield their energy to restore and maintain the vitality of decadent tissues. A vision thus comes to us of a new chemistry with limits far flung beyond those which constrain our knowledge of to-day, a

chemistry which will embrace and co-ordinate not only the properties of inanimate matter upon this earth, not only the wondrous mechanism of the life of man in health and in disease, but in addition the stupendous marvels of the birth and growth of the worlds outside our own. From those who would decry this as a mere speculation I beg forgiveness, and plead that speculation based on sure experimental fact is the life blood of true scientific research.

[E. C. C. B.]



Friday, March 16, 1928.

SIR ROBERT ROBERTSON, K.B.E. M.A. F.R.S., Honorary Secretary  
and Vice-President, in the Chair.

EDMUND T. WHITTAKER, LL.D. Sc.D. F.R.S.,  
Professor of Mathematics, University of Edinburgh.

### The Quantum and Relativity Theories of Light.

THE classical theory of light, which was created by Fresnel in 1816-23, and was transformed into an electromagnetic theory by Maxwell in 1861-62, was believed, at the end of the nineteenth century, to be capable of accounting for all optical phenomena. Since then, however, a number of phenomena have been observed which appear to be irreconcilable with it, at any rate in the form in which it is usually presented. These phenomena relate to the transfer of energy between radiation on the one hand, and atoms of matter on the other. For example, when X rays fall on a metallic plate, electrons are set free and ejected from the plate with definite velocities: in this "photo-electric" effect, the velocity with which each electron is endowed at its liberation is altogether independent of the intensity of the X-rays, and depends only on their frequency. When the X-rays are feeble in intensity, we are bound to suppose that, in order to acquire this velocity, the electron has somehow been enabled to collect energy from a large area of the cross-section of the incident beam. But it was shown by the late Lord Rayleigh that on the principles of the classical theory, the area of a wave-front of light of wave-length  $\lambda$  which can be tapped and have its energy extracted by a small resonator is something comparable with  $(\lambda^2/\pi)$ ; and this is altogether inadequate to explain the experimental results. We must therefore conclude that the classical theory fails to account for the phenomena.

As an alternative hypothesis it was suggested by Einstein in 1905 that light may be concentrated in very small parcels or "quanta," which retain their energy undiminished as they travel out into space, without the unlimited spreading which takes place with ordinary diverging waves: the atom would then be supposed to capture a whole quantum at once and absorb its energy, which is of amount  $h\nu$ , where  $h$  is Planck's constant, and  $\nu$  is the frequency of the light. This hypothesis accounts satisfactorily for photo-electric phenomena, and also for the charge of wave-length of X-rays due to scattering (the Compton effect), and the production of recoil electrons.

The hypothesis that light travels in small compact parcels may, however, be reconciled with the classical electromagnetic theory, if we assume that the parcels contain electric or magnetic charge which is travelling with the velocity of light; in fact, the field surrounding electric or magnetic charge travelling with the velocity of light has all the ordinary classical properties of light, except that of spreading; the energy of the field remains permanently linked up with the moving charge, so that an atom which captures the moving charge thereby captures all the luminous energy associated with it.

This way out of the difficulty was, until quite recently, open to the objection that, while it accounted satisfactorily for the propagation of light through free space in non-spreading quanta, it did not help in any way to clear up the apparent contradictions between the classical theory and Bohr's theory of the emission of spectra. According to the classical theory, we should expect that radiation of frequency  $\nu$  would be produced by an electron, or electronic system, vibrating or performing an orbital revolution, with the same frequency  $\nu$ . But in Bohr's theory, which has been remarkably successful in explaining spectra, monochromatic radiation is produced when an electron within an atom falls from an orbit, in which its energy is (say)  $H_1$ , to another orbit in which its energy is (say)  $H_2$ , the frequency  $\nu$  of the radiation being determined by the relation

$$h\nu = H_1 - H_2;$$

so that in Bohr's theory, the frequency of the emitted radiation is quite different from the frequency of the oscillations or revolutions taking place in the atom. This discrepancy has attracted a tremendous amount of attention during the last fifteen years, and has led some physicists to speak somewhat hastily about the "failure" of the classical theory. Within the last two years however, this particular trouble has been removed, and a complete reconciliation with the principles of the classical theory has been effected, by means of Schrödinger's wave-mechanics, the argument being as follows:

In Schrödinger's theory the phenomena are described in terms of a "wave-function"  $\psi$ , which satisfies a certain partial differential equation—just as the vibrations of a violin string may be worked out mathematically by means of a function which represents the displacement of a particular point of the string at a particular instant of time, and which satisfies a partial differential equation. In the case of the violin string we know that there are certain special solutions of the partial differential equation which represent particularly simple states of vibration of the string—which represent, in fact, the pure fundamental note and its various overtones; similarly, in the case of Schrödinger's wave-function, there are certain particular solutions of the partial differential equation for  $\psi$ , which correspond to what in Bohr's theory were pictured as the "stationary states" of the atom. There is, however, this great difference between Bohr's

original theory and Schrödinger's theory, that in Bohr's theory a stationary state meant a particular kind of orbital motion, so that an atom could be in only one stationary state at one time; whereas, in Schrödinger's theory the various stationary states can be superposed (since they are merely different particular solutions of a linear partial differential equation), just as overtones can be superposed on the fundamental tone of a violin string; and this makes all the difference when it comes to reconciling our ideas with those of the classical theory.

Suppose then that we consider an atom in one of Schrödinger's stationary states, so that the wave-function  $\psi$  involves the time  $t$  through a factor  $e^{2\pi i\nu_1 t}$ . The electric moment of the atom is the integral of  $\psi \bar{\psi}$ , when  $\bar{\psi}$  is the complex quantity conjugate to  $\psi$ , this integral being integrated in a certain way over the atom. Now since  $\psi$  contains the factor  $e^{2\pi i\nu_1 t}$ , it follows that  $\bar{\psi}$  will contain the factor  $e^{-2\pi i\nu_1 t}$ , and therefore in the product  $\psi \bar{\psi}$  these factors will destroy each other: that is to say, when the atom is in one of Schrödinger's stationary states, its electric moment does not vary with the time, and therefore, *according to the classical theory*, it will not emit radiation.

Suppose next, however, that the atom is not in a pure stationary state, but is in a state which is represented by the superposition of two stationary states, for which the wave-function has the time-factors  $e^{2\pi i\nu_1 t}$  and  $e^{2\pi i\nu_2 t}$  respectively, so that

$$\psi = A e^{2\pi i\nu_1 t} + B e^{2\pi i\nu_2 t},$$

where  $A$  and  $B$  do not involve the time. Then we have

$$\begin{aligned} \psi \bar{\psi} &= (A e^{2\pi i\nu_1 t} + B e^{2\pi i\nu_2 t}) (\bar{A} e^{-2\pi i\nu_1 t} + \bar{B} e^{-2\pi i\nu_2 t}) \\ &= A \bar{A} + B \bar{B} + A \bar{B} e^{2\pi i(\nu_1 - \nu_2)t} + B \bar{A} e^{-2\pi i(\nu_1 - \nu_2)t}, \end{aligned}$$

and hence the electric moment of the atom will be periodic, with frequency  $(\nu_1 - \nu_2)$ ; and consequently the atom, *according to the classical theory*, will emit radiation of frequency  $(\nu_1 - \nu_2)$ . This radiation will continue until the consequent exhaustion of energy has again reduced the atom to a single pure stationary state.

If  $E_1$  and  $E_2$  are the energies associated with the two stationary states, then  $E_1 = h\nu_1$  and  $E_2 = h\nu_2$ , so the radiation is of frequency  $\frac{1}{h} (E_1 - E_2)$ , just as in Bohr's theory; but this result has now been obtained by what are essentially classical methods—by the old classical theory of the normal solutions of partial differential equations—and without doing any violence to the electromagnetic theory of light. The classical theory, in short, has swallowed up the quantum theory.

I do not wish to be understood as expressing the opinion that the

present state of Schrödinger's wave-mechanics is definitive and final. It seems to me that certain modifications will have to be made in it in the near future, in particular the replacing of Schrödinger's single scalar wave-function  $\psi$  by a vector or tensor of some kind. But it is a very great advance on anything that has preceded it; and the remarkable experiments of Davisson and Germer in America, and of G. P. Thomson in this country, on the scattering of cathode rays have substantiated beyond doubt its leading idea, that there is something of an undulatory character associated with a beam of electrons.

It seems probable that before long the two most interesting branches of modern theoretical physics—wave-mechanics and general relativity—will make approaches towards each other, and tend to become fused in a more comprehensive doctrine. Meanwhile, from the side of relativity, some progress has been made in studying the influence of gravitation on electromagnetic phenomena—an influence which may be of importance in the nucleus of an atom. It is now recognised that a gravitational field is accompanied by, or (perhaps we should say) consists in, a “curvature” or “distortion” of space, which, if the gravitational field is sufficiently intense, can have a remarkable influence on any electromagnetic phenomena which may be taking place there. This influence resembles in a general way that which would be observed if the dielectric constant and magnetic permeability varied from point to point of space, giving rise of course to an apparent variation of the refractive index. The only case in which effects due to this cause have been actually observed is the famous case of the deflection of the rays of light from stars in passing close to the gravitating mass of the sun, a phenomenon which was predicted by Einstein and measured on the plates taken at the eclipse of May 1919. The solar deflection is very small; but it is possible that in the intense gravitational fields inside the nucleus of an atom, electromagnetic phenomena may be more powerfully modified. Certainly the most remarkable happenings are possible in theory; thus, a ray of light can describe a circular path, returning into itself; and in other ways luminous energy may, by the mere distortion of space, be confined perpetually to a small definite region of space, just as if it were confined in a box with reflecting sides. The capture of a ray of light by a gravitating centre may be studied mathematically; and amongst other results it is found that radiation is emitted by an electron which is permanently at rest, provided it is placed in an alternating gravitational field. The knowledge that a motionless electron may radiate, while (as a natural consequence) an accelerated electron does not necessarily radiate, in a gravitational field, may prove useful in accounting for the behaviour of electrons in atoms. But whether it will or not, time alone can show.

[E. T. W.]

Friday, June 8, 1928.

SIR ROBERT ROBERTSON, K.B.E. M.A. F.R.S., Hon. Secretary  
and Vice-President, in the Chair.

GEORGE P. THOMSON, M.A.,  
Professor of Natural Philosophy, University of Aberdeen.

### The Waves of an Electron.

THE history of the newer physics, as it may be called, is largely the history of the very successful attempts which have been made to explain the facts of the physical universe in terms of electricity. In particular, the natural units of electricity, the electron first isolated as the carrier of the negative charge in the cathode rays, and the more massive proton with its equal positive charge, have been the bricks out of which physicists have tried to build model atoms. But until recently the only properties which could be attributed with certainty to the electron were its mass,  $9 \times 10^{-28}$  gram., and its charge,  $-4.77 \times 10^{-10}$  electrostatic units. It is indeed possible to calculate a "size" on the assumption that it follows the same laws as a charged metal sphere in a laboratory, but the value found,  $3.7 \times 10^{-13}$ , is neither confirmed nor contradicted by any experimental evidence.

To show, as I hope to do to-night, why we are now obliged to ascribe much more complicated properties to the electron, I must make a digression into optics, as it was from this direction that the theory comes which lead to the experiments I have to describe. It is well known that there are a number of phenomena which are instances of wave-motion in what used to be called the ether, though it seems now more fashionable to call it space. Such are wireless waves, light, ultra-violet radiation, X-rays. They differ only in wave-length, and it is convenient to refer to them all as light.

Now at the beginning of the century the wave theory of light was one of the most firmly established parts of physics. It is true that for many purposes light was treated as consisting of rays, i.e., effects travelling in a straight line, but this was merely an approximation used for convenience in calculation, and not regarded as of any great physical significance. The evidence for waves (interference and diffraction) was, and remains, overwhelming. Gradually, however, a series of experimental and theoretical results accumulated which showed that this was not the whole story, and in particular that light could communicate an amount of energy to an electron which only depended on the *kind* of light and not at all on the *intensity*. If light consists of continuous waves this seems almost impossible; but it is just what we should expect if, as Newton firmly held, light is due to a stream of corpuscles. In such a case if one of these hit an electron it would give to it an energy which would be quite independent of the number of other corpuscles present in the stream, i.e., of the intensity of the light.

Prince Louis de Broglie has hit on a brilliant synthesis of the two views. Put very briefly it comes to saying that light is indeed corpuscular, but that the corpuscles are accompanied and guided by waves. Now the bearing of this on our subject is as follows: de Broglie's theory is quite a general one, and should apply to *any* sort of corpuscular motion, in particular electrons should be accompanied by waves which determine their motion. It would seem at first sight that this would involve a contradiction with what is already known about the motion of electrons. For example, waves spread after passing through a small aperture, while electrons can be concentrated into a fine beam by a tube or series of slits. But it is all a question of wave-length. Ordinary visible light only spreads very slightly round obstacles because its wave-length is small compared with the size of ordinary objects. Wireless waves bend much because their wave-length is large.

There is in fact a relation pointed out more than a century ago by Hamilton between optics and dynamics. The laws of dynamics in their most general expression, the principle of action, are mathematically identical with Fermat's principle which is the most general statement of optics on the ray theory. Now in optics rays are an approximation to the wave theory, more and more nearly true the smaller the wave-length: perhaps the accepted mechanics of Newton and Hamilton is also only an approximation, true in practice because the wave-lengths concerned are very small? If so, we must develop a new mechanics to deal with cases when the wave-length is not of negligible size.

To-night I shall only speak of the mechanics of a free electron. Earlier in the year the Institution had the privilege of hearing from Professor Schrödinger an account of the rapid progress that has been

made with the wave-mechanics of the electrons inside the atom, a progress mostly due to Professor Schrödinger himself.

De Broglie's results are as follows :—For any moving particle the wave-length  $\lambda = h/(\text{momentum})$  where  $h$  is Planck's constant  $= 6.58 \times 10^{-27}$ . This in fact comes out negligibly small for any ordinary body. Even for an electron moving with the moderate energy of 150 volts it is  $10^{-8}$  cm., or about that of a soft X-ray while for cathode rays of, say, 15,000 volts it is  $10^{-9}$  cm.

Still, Sir W. Bragg and his son have shown us how to measure the wave lengths of X-rays, small though they are, and the electron waves may yield to a similar treatment.

We must first consider some general properties of these waves. According to de Broglie the speed of the waves,  $V$ , is  $c^2/v$ , where  $v$  is the speed of the particle, and  $c$  the velocity of light. They are thus faster than light. This result would be contrary to relativity if the waves carried energy, and so could transmit a signal, but as the energy is supposed associated only with the *particle* this objection does not come in; indeed, on the classical optical theory, cases are known of metals, such as sodium, having a refractive index less than unity, which implies a wave velocity greater than  $c$ . From the above two equations, taking account of the variation of mass with speed,  $V^2 = c^2 + \frac{m_0^2 \lambda^2}{h^2 c^4}$ , and so depends on  $\lambda$ . Thus there is *dispersion*, in the optical sense, for these electron waves even in free space.

The late Lord Rayleigh showed that in such a case, besides the velocity of the independent waves, there is what he called a *group velocity*, which is the speed with which the pattern formed by the superposition of several waves of slightly different wave-length moves along. Now an application of his formula shows that in this case the group velocity is precisely  $v$ , the speed of the electron, so that the electron carries its *group* with it (or the group carries the electron, if you prefer it), though the individual waves composing the group are perpetually shooting through from behind.

Again, since an electron is charged, its motion is affected by an electric or a magnetic field. On the older view of an electron this was simply a consequence of the laws of electricity. On the new view the electron goes where its wave takes it. Somehow the only possible paths are those along which the wave is propagated. On this view the change in motion of the electron is analogous to the change in direction of a ray of light when it enters a refracting medium. In fact, by choosing the field in an appropriate manner, we can imitate the effect on light of a corresponding piece of glass. For example, we can make a field equivalent to an ordinary convergent lens and bring electrons to a focus.

But, of course, this is only a translation between one view and the other. To test the new theory we must use something which has a

regular structure comparable in size with the supposed wave-length. Here the wide experience obtained with X-rays comes to our aid, and the natural regularities of a crystal give what is needed. The regularly spaced atoms of a crystal each scatter the waves, since they scatter the electrons. Such a system of regularly arranged scattering points produces, as is well known, a peculiar effect on a simple wave, which is deflected into a few definite directions. It forms, in fact the three dimensional analogue of the ordinary optical ruled diffraction grating. The effect can be illustrated in its simplest form with waves on a liquid.

The idea of using a crystal in this way has been carried out by Davisson and Germer in America, and by Reid and myself in this country. As my time is limited, you will, perhaps, pardon me if I limit my description to our work, especially as Davisson's and Germer's experiments lead to the same general conclusions. As the atoms of a crystal are arranged in three dimensions, the result is somewhat more complicated than in the experiment you have just seen. If a beam of X-rays is passed through a single crystal and allowed to fall on a photographic plate, the developed picture is a series of spots whose position depends on the structure of the crystal. If it passes through a powder formed of a large number of very small crystals arranged at random the spots due to each tiny crystal join together to form a series of concentric rings, whose relative sizes depend on the crystal structure, the absolute size of the whole pattern being proportional to the wave-length of the X-rays. Both these methods, or their equivalent, have of course been extensively used in the investigation of crystal structure by X-rays, nowhere more successfully than in this Institution.

The apparatus we have used is a direct application of this method to the study of electrons.

It is necessary to use very thin films because electrons have vastly less penetrating power than X-rays, and they must not only penetrate the film, but be so little affected by it that the scattering is what is technically called "single." In practice this means that only a small minority should be appreciably scattered at all. The films we used were only a few millionths of a cm. thick, in fact it is no use trying a metal film unless it is thin enough to be transparent. Some of the metals show uniform rings, others spots arranged round rings. Both can be paralleled in the analogous results with X-rays.

In comparing theory with experiments we have three separate checks. First, the relative sizes of the rings must conform to the known crystal structure. For the metals I used these go as the square roots of certain integers. In fact, the first few rings should be in the ratio  $\sqrt{3} : \sqrt{4} : \sqrt{8} : \sqrt{11} : \sqrt{12} : \sqrt{16} : \sqrt{19} : \sqrt{20}$ . The following table shows the extent of the agreement.



## RELATIVE DIAMETER OF RINGS.

Metal . .	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{8}$	$\left\{ \begin{smallmatrix} \sqrt{11} \\ \sqrt{12} \end{smallmatrix} \right\}$	$\sqrt{16}$	$\left\{ \begin{smallmatrix} \sqrt{19} \\ \sqrt{20} \end{smallmatrix} \right\}$	$\sqrt{24}$	$\sqrt{27}$	$\left\{ \begin{smallmatrix} \sqrt{35} \\ \sqrt{36} \end{smallmatrix} \right\}$
Gold . .	$\sqrt{2.93}$ $\sqrt{3.05}$ $\sqrt{2.96}$	$\sqrt{4.02}$ $\sqrt{4.05}$ $\sqrt{4.08}$	8.00 8.00 8.00	$\sqrt{11.2}$ $\sqrt{11.4}$ $\sqrt{11.2}$		$\sqrt{19.8}$ $\sqrt{19.1}$ $\sqrt{19.5}$		$\sqrt{22.7}$ $\sqrt{26.6}$	$\sqrt{35.4}$
Aluminium		$\sqrt{4.00}$ $\sqrt{3.98}$ $\sqrt{4.02}$	8.00 8.00 8.00	$\sqrt{10.9}$ $\sqrt{11.0}$ $\sqrt{10.9}$	$\sqrt{16.5}$ $\sqrt{15.7}$ $\sqrt{15.9}$	$\sqrt{20.4}$ $\sqrt{21.2}$ $\sqrt{19.4}$		$\sqrt{27.0}$ $\sqrt{27.8}$ $\sqrt{26.8}$	$\sqrt{35.0}$
Platinum	$\sqrt{3.00}$ $\sqrt{3.07}$ $\sqrt{3.04}$	$\sqrt{4.00}$ $\sqrt{4.01}$ $\sqrt{4.03}$	8.00 8.00 8.00	$\sqrt{10.9}$ $\sqrt{11.3}$ $\sqrt{11.2}$	$\sqrt{15.3}$ $\sqrt{16.4}$	$\sqrt{18.4}$ $\sqrt{19.0}$	$\sqrt{24.0}$ $\sqrt{23.4}$	$\sqrt{26.5}$ $\sqrt{27.1}$	$\sqrt{35.0}$

Secondly, if L. Broglie's Theory is true the wave-length is inversely as the momentum, i.e., apart from a small relativity correction the product of the diameter of any one ring into the square root of the measured energy of the rays should be constant.

Aluminium.		Gold		Platinum	
Voltage.	D $\sqrt{P}$	Voltage	D $\sqrt{P}$ .	Voltage	D $\sqrt{P}$
21,800	(359)	21,000	(344)	18,200	(379)
34,500	385	33,700	377	25,500	395
45,000	385	44,000	377	34,500	420
57,600	395	55,000	379	40,000	401
64,000	385	58,000	376	45,000	413
Means	387		377		407

## Celluloid.

Voltage	D $\sqrt{P}$ .	Voltage	D $\sqrt{P}$ .
9,800	185	23,200	193
11,500	175	30,500	186
16,100	189	36,000	193
16,800	191	42,500	189
21,000	190	50,000	195

Thirdly, the actual size of the rings is calculable from the assumed wave-length, and the known spacing of atoms in the crystal. The best ways of showing the agreement is to work back, calculating the crystal spacing from the experiments and theory, and comparing with that found by X-rays.

SIZE OF CRYSTAL UNIT.

		Aluminium.	Gold.	Platinum
X-ray measurements	measurements	$4.046 \times 10^{-8}$	$4.06 \times 10^{-8}$	$3.91 \times 10^{-8}$
Cathode ray	measurements	$4.06 \times 10^{-8}$ $4.00 \times 10^{-8}$	$4.18 \times 10^{-8}$	$3.88 \times 10^{-8}$ $3.89 \times 10^{-8}$

Finally, in a few cases the individual spots can be used. This is when the small area struck by the rays happens to consist wholly or mainly of a single crystal. In such a case we can find the orientation of the crystal from some of the spots and see if the others check.

I think that this agreement may be regarded as establishing the essential truth of the theory.

But there remain great difficulties of interpretation. What are these waves? Are they another name for the electron itself? How many waves in series does an electron have? What is the relation between the electron waves and those of light and X-rays? Some of these questions I should like very briefly to discuss, but I must warn you that we now leave the sure foothold of experiment for the dangerous-but fascinating paths traced by the mathematicians among the quicksands of metaphysics. First, as to the length of the train of waves. Here we have a little direct evidence. The sharpness of the rings depends, among other things, on this length. A short train of waves results in blurred rings. If we suppose the whole width of the rings due to this, I calculate from the fact that it is just possible to separate the  $\sqrt{11}$  and  $\sqrt{12}$  rings that there must be at least 48 ordered waves in the series. Probably there are many more, as several other causes tend to widen the rings. But this may only apply to my particular experimental arrangement. Theoretically it seems probable that an exact knowledge of the speed of an electron implies that it has an infinite wave-train associated with it, just as ideally monochromatic light implies an infinite train of light waves. Since there cannot actually be an infinite wave-train this means that an electron's speed can never be exactly known, which in one sense is not surprising, for all measurement is approxi-

mate, and it can be shown that the conditions under which the velocity of an electron could be found with great accuracy are precisely those in which a long train of waves could accompany it. But suppose we have a short train of waves. The velocity is uncertain. Is this because there are really many electrons concerned and they have different velocities? In most of the experiments one could devise there would be, but I don't think this covers all cases.

Imagine a small speck of radio-active material which emits electrons as fast  $\beta$  rays. If you make it small enough the particles may follow each other at intervals of minutes, or days, or years, if you like. It seems impossible to suppose that these electrons have any connection with each other. They come from different atoms at widely different times. One is forced to the conclusion that each must have its own separate wave system. But this wave train must be finite, probably in fact it is rather short, and one reaches the surprising conclusion that the electron *has* no definite velocity, even though it may be moving in force-free space. This raises obvious difficulties about energy which I do not pretend to be able to solve, but the work of Ellis and Worster on Ra.E. seems to show that there is an uncertainty of this kind, which is in fact of about the right amount.

As regards the relation between electron waves and light waves: they are certainly not the same, even when their wave-lengths are equal. They go at different speeds: one is refracted by electric and magnetic fields, while the other is not, their penetrating powers in ordinary matter are widely different. If they are the actual motion of an "ether" it must differ in some way in the two cases.

My father, Sir J. J. Thomson, has shown that the relation between wave-length and velocity of the electron waves is precisely that which holds for light waves in a medium containing free electric charges. The properties of such a medium have recently become of great importance, for the possibility of long distance wireless has been shown to be due to the existence of a region with these properties in the upper atmosphere. It is tempting to regard this agreement as something more than a mere coincidence, and to consider the waves of the electron as waves in an ether modified by the presence of the tubes of force, which since the days of Faraday many physicists have regarded as having a real existence round an electric charge. Thus the electron would provide, not indeed its own ether, but the necessary modification of that ether.

But I should like also to suggest another possibility, though you may perhaps think it rather a cowardly way out of the difficulty.

Personally I see no necessity for there to be any vibration of a material or quasi-material object. The essence of a wave is the transference of a *state* according to certain laws, for example, a "heat wave" crossing the Atlantic. The state may, or may not, be one of motion. On this view the function of the waves is to produce

conditions at the electron which oblige the latter to move along the instantaneous position of the wave-normal (in the absence of a magnetic field), and along another, but determinate, direction in a magnetic field. But though it seems possible to regard the motion of the electron as determined by the wave in its immediate neighbourhood, it must never be forgotten that the direction of each part of a wave-front depends on the history of the whole wave-front. Any circumstance that influences one part of a wave influences the whole, and this is of the essence of wave motion. The electron is influenced by conditions at a distance, but indirectly through its waves. Thus in our experiments the electron is influenced not merely by the nearest atoms of the crystal, but by the whole of the crystal which is exposed to the beam. The *width* of the wave-front must be taken as the cross-section of the tube through which the electrons pass.

But although the whole wave-front, in theory, affects the electron, all parts do not affect it equally. Thus, suppose the width of the beam were diminished by gradually reducing the size of the tube, apart from the obvious diminution in intensity, the only effect would be a diminution in resolving power due to the reduction in the number of grating elements. When the resolving power is large a considerable change, such as is produced by halving the number of atoms affected, produces comparatively little change in the pattern of the diffracted rays, i.e., the distribution of scattered electrons.

The main features of the pattern are determined by the first few elements, just as, on the older view, the direction of the scattered electron would be mostly determined by the forces exerted on it by the atoms near which it goes and comparatively little by the more distant ones.

The easiest way of looking at the whole thing seems to be to regard the waves as an expression of the laws of motion. The uniform motion of Newton's first law is replaced by a simple plane wave, and so on. On this view, the electron remains the reality, and this seems right, for after all it is the electron as a particle which is actually detected in any conceivable experiment, and the waves come to bear the same sort of relation to it that Newton's or Einstein's law of gravitation bears to the planets which obey it.

It is remarkable how near this view comes to that proposed by Newton in the case of Light, which as we have seen is analogous, and I can hardly give a better statement of the position, allowing for slight changes in terminology, than by quoting what he says :—

"Those that are averse from assenting to any new discoveries but such as they can explain by an hypothesis, may for the present suppose, that as stones by falling upon water put the water into an undulatory motion, and all bodies by percussion excite vibrations in the Air; so the Rays of Light, excite vibrations in the refracting

Medium or Substance . . . that the vibrations thus excited are propagated in the refracting or reflecting Medium or Substance, much after the manner that vibrations are propagated in the Air for causing Sound, and move faster than the rays so as to overtake them . . . and that every Ray is successively disposed to be easily reflected or easily transmitted, by every vibration which overtakes it But whether this Hypothesis be true or false I do not here consider."

In what follows he contents himself by describing the experimental facts. But his hypothesis, the guess of genius, after a century of discredit, is reasserting its superiority over the more logical, but less inspired, ideas of the early nineteenth century.

[G. P. T.]

Friday, January 18, 1929.

SIR ROBERT ROBERTSON, K.B.E. D.Sc. LL.D. F.R.S., Secretary and  
Vice-President, in the Chair.

SIR WILLIAM BRAGG, K.B.E. D.Sc. F.R.S. M.R.I.,  
Fullerian Professor of Chemistry.

### Further Progress in Crystal Analysis.

[ABSTRACT.]

ALLOYS have played a great part in the history of mankind. The qualities of pure metals are rarely desirable, but the properties of alloys cover a far wider range, within which can be found every variety of usefulness. Pure copper is too soft for most purposes, but when varying quantities of tin are introduced the bronzes so formed have many applications. At one stage of human development bronze was all-important. It is still largely used. The copper coinage is only slightly alloyed; the useful "gun-metal" contains a larger quantity of tin, bell-metal contains more, and speculum or mirror-metal more still. Small quantities of other substances, especially zinc, are often inserted into bronzes; and the influence of minute quantities of such foreign substances is remarkable. Since many substances can be used in making alloys, two or more at a time, and since even minute quantities of a component often change the properties entirely, it will readily be understood that the possible variations are almost infinite. Among these metallurgists seek for those which can be put to practical use. Great advances have been made in recent years, and such terms as chrome steel, manganese steel, duralumin and the like, have become common.

The reasons for this variety are most obscure, and great interest attaches to any method which can help to bring order and understanding into the complexity. The X-rays have come to give assistance of a novel kind. They reveal the modes in which the atoms are arranged in solid substances, provided that any regularity of arrangement exists, and in general this is the case. It turns out that the atoms in the different phases of a mixture are put together according to different patterns, and the properties of the substances are obviously connected with the pattern. In pure copper the atoms

are piled together in close packing, like spherical shot; each sphere then touches twelve neighbours. When a small number of zinc atoms are added they distribute themselves at random amongst the copper atoms without disarranging the pattern very much. But there is a limit to this addition. If too much zinc is put in a new pattern is formed, in which each atom now has only eight neighbours. Next comes a remarkable change as more zinc still is put with the copper. A very complicated pattern is formed of which the unit is twenty-seven times as large as in the preceding case, and there are fifty-two atoms in it. This alloy is very hard and brittle. Curiously enough there is an alloy of copper with aluminium, and again of copper with tin, in which the same properties are exhibited, the same pattern is found, and the same number of atoms in the pattern. Moreover, what is still more interesting is that there is the same number of free electrons. The free electrons are those which a metal can shed comparatively easily: a zinc atom can shed two, an aluminium atom three, and a tin atom four. These curious alloys are composed of five atoms of copper to eight of zinc, nine of copper to four of aluminium, and the third, very approximately, in the ratio of thirty one of copper to eight of tin. In each case there are thirteen atoms and twenty-one electrons.

These new results, which are most interesting from all points of view, are due mainly to the work of Owen and Preston, Bradley, and Bernal in England, Westgren and Phragmen in Sweden. They open up new ideas of the conditions in the alloy. They suggest that we ought not merely to think of an alloy as a mixture of atoms, but in some cases at least as a mixture of electrons with atoms, the latter having considerable latitude as to nature.

Somewhat similar conclusions have been reached in regard to the silicates composing by far the major part of the earth's crust. We are getting away from the conception that the "molecule" of liquids and gases is generally to be found in all solids.

In a different direction an important step forward has been made in Mrs. Lonsdale's (Miss Yardley) determination of the disposition of the atoms in the organic compound hexamethyl benzene. The application of the X-ray methods to organic structures has always been very tempting, because the properties of the organic molecule depend so remarkably on the mutual arrangement of the atoms of which it is composed. This has of course been long known, and it has been found possible to arrive at some knowledge of the particular designs by studies of the chemical reactions peculiar to them. But the X-rays may be expected in the end to furnish quantitative, as against qualitative, details of the molecular structure, and to give the relative positions of the atoms in space. The long chain compounds, which constitute a very important section of the organic substances, have already been attacked with success, but the other important section, consisting of substances founded on the benzene ring, have

not hitherto proved so amenable. They are more complicated, and their analysis is more difficult. If any one of them can be worked out in detail the whole problem will be simplified. It appears that Mrs. Lonsdale's solution in the case of hexamethyl benzene has actually provided this initial success. The molecule consists of the hexagonal benzene ring of carbon atoms, to each of which is attached a methyl group ( $\text{CH}_3$ ). The unit of pattern contains only one molecule. It is triclinic, that is to say, there are no planes or axes of symmetry; there is, however, a centre of symmetry. As there is only one molecule in the unit cell, this centre is found in the molecule itself, the only symmetry which it possesses. In certain ways the cell very nearly possesses other symmetries, and by a skilful use of these approximations as measured by the curious effect which they have on the relative intensities of reflection by different sets of planes within the crystal, Mrs. Lonsdale has been able to place every carbon atom in the molecule. The result gives a picture of the molecule resembling even more closely than is usual in these cases the diagram of the chemist, except of course that the symmetry is not quite so perfect as the diagram shows. All the carbon atoms are in one plane. It is now to be expected that the way is made easier for attempts to solve the structures of other organic substances of the same important group.

[W. H. B.]



Friday, February 15, 1929.

SIR ROBERT ROBERTSON, K.B.E. F.R.S., Secretary and  
Vice-President, in the Chair.

ERIC K. RIDEAL, M.B.E. D.Sc. M.R.I.

### Chemiluminescence.

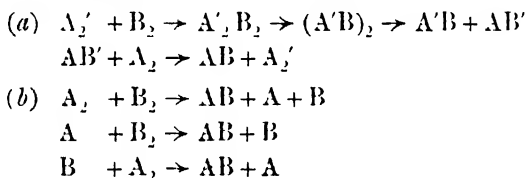
IN attempting to make the subject matter of this discourse as experimental as possible it will be impossible to delve in great detail into the molecular mechanism of the reactions. This, I think, is as well, because many of the reactions which should be shown on account of their great beauty are certainly extremely complicated, and have not, in fact, been subjected to any but a very superficial examination.

Chemiluminescence may be regarded as the counterpart of photochemical processes. By the absorption of light of suitable frequencies atoms and molecules may be raised to states of higher initial energy. These excited entities may now undergo a series of changes, the nature of which will depend on a variety of circumstances. They may liberate their absorbed energy in the form of fluorescent light, impart part or all of their energy by a collision to a neighbour of another species, become converted into a metastable more permanent and energy rich molecule, which may subsequently revert back into the normal form, or suffer some species of chemical reaction such as ionisation, dissociation or combination.

By suitable modification of conditions one can affect the velocities of chemical reactions over relatively wide ranges, and it is found that in many strongly exothermic reactions there exists a narrow range of relatively high velocities which is chemiluminescent. Closer examination indicates that practically all these reactions are complex, in that they are accompanied not only by the emission of radiation localised in some portion of the spectrum, but also by a rise in temperature. It is by a study of the chemiluminescent portion of such composite reactions that we may hope to gain a further insight into the molecular mechanism and the operation of the process of chemical activation. We may with some degree of assurance assume that chemiluminescence is in many cases the result of liberation of chemical energy in a form similar to that of fluorescent energy, and we have noted that fluorescence is the result of decay of a number of excited molecules, the excitation being produced in this case by the absorption of radiation.

Thus conditions suitable for chemiluminescence result in reactions in which large numbers of excited molecules are produced by chemical reaction, under conditions such that at least a fraction of the excited molecules can revert to the normal form with the emission of radiation. Excluding thermally accelerated exothermic reactions, a large group of auto-accelerating reactions exhibit chemiluminescence; these are usually designated as branching chain reactions, and we shall observe that there are several hypotheses as to the nature of such reactions, and at least two distinct light-producing processes.

A typical reaction of this type is the oxidation of phosphorus, one of the oldest chemiluminescent reactions observed with a definite substance. Although the chemiluminescence of fireflies, decaying wood, and certain bacteria and fish have long been commented on, and were formerly attributed to the action of vital forces. The name phosphorus arose from a confusion of chemiluminescence with the phosphorescence of the impure barium sulphide, the so-called *lapis Bologniensis*. We may symbolise the fact that the reactions proceed in branching chains in a number of ways; thus, denoting the reactants by  $A_2$  and  $B_2$  and the molecules in the excited state by  $A_2'$ , we might postulate as the mechanism :-



In both cases the conditions that one elementary reaction shall produce at least two reacting molecules, so as to effect an auto-accelerated reaction, are fulfilled, but whilst in the first the chemiluminescence is imagined to result from the return of the excited species  $AB'$  or  $A_2'$  to the normal, in the second it is supposed to take place through some type of atomic combination, e.g.  $2A \rightarrow A_2$  or  $A + B \rightarrow AB$ , a mechanism which has been more fully investigated in a series of reactions which we shall have occasion to discuss later.

We may note that in addition to these types of chain mechanism there exists a third, in which it is imagined that a certain number of reaction centres are formed, by some identified as ions; around these reaction centres reaction takes place, and more reaction centres are formed. As a hypothetical case we might imagine that in a hydrogen chlorine mixture a positive ion is formed; around this ion a number of hydrogen and chlorine molecules are held by electrostatic forces. On neutralisation of the ion the energy set free effects the combination of the small group of molecules around the ion, chemiluminescence and the formation of a few more ions results.

That in the oxidation of phosphorus and of sulphur, and probably many other substances, the chemiluminescence is the result of some such type of chain mechanism can scarcely be doubted, but it is difficult in fact to state to which of these three possible types any one reaction definitely belongs. It is perhaps significant that in the oxidation of phosphorus a number of the lines in the complex band spectrum of the emitted light are identical with those of ionised oxygen. A typical phenomenon observable in the chain or cluster reactions is that of inhibition by small quantities of inhibitors. We may note the ease with which inhibitors such as benzene and ether inhibit the glow of phosphorus, a confirmation of the nature of the chemical process at work. Many other vapours exhibit chemiluminescence on oxidation, a fact noted by Sir H. Davy: thus the vapours of ether and carbon disulphide can readily be caused to undergo cold luminous combustion. Under more restricted conditions the union of acetylene and chlorine and the oxidation of the hydrocarbons can be made to exhibit chemiluminescence, and although in these reactions the thermal changes are relatively large, yet since the light emitted is definitely chemiluminescent it seems almost certain that, contrary to the views of several investigators, in these reactions, one cannot be dealing exclusively with thermally accelerated as opposed to branching chain or cluster accelerated reactions; excited molecules, atoms or reactive centre clusters must be taking part in the reaction.

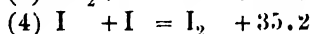
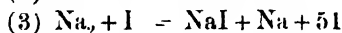
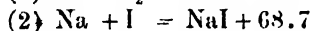
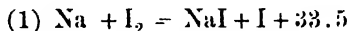
Far more complicated but equally beautiful are a number of chemiluminescent reactions taking place in solution. The absence of a draught-chamber precludes one from showing the well-known Wedekind reaction, the interaction of chloropierin and phenyl magnesium iodide exhibiting a green chemiluminescence; but the cold oxidation of pyrogallol formaldehyde mixture exhibiting an orange-red light, due to Trautz and Schorigin, blue luminescence in the oxidation of three aminophthalic hydrazide, and the green of triphenyl glyoxalin (Lophin), are all brilliant and readily demonstrated. These reactions are characterised by a high temperature coefficient, some 2-3 for a rise of  $10^{\circ}\text{C}$ ., an indication of the chemical origin of the light-emitting system.

It is somewhat remarkable that few people have observed the beautiful chemiluminescence exhibited by the interaction of chlorine or chromyl chloride with ammonia, although I suppose the former reaction is demonstrated annually in at least one of the classes in all schools where chemistry is taught.

Sir James Dewar, in this Institution, noted a chemiluminescence when ozone was brought into contact with organic matter. Such chemiluminescence is particularly marked in the oxidation of certain dyestuffs both fluorescent and non-fluorescent; we may observe the phenomenon in a brilliant form in the case of alcoholic solution of both eosin and safranin. The chemiluminescent light is not identical

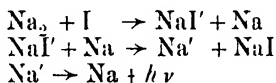
with the fluorescent light of these dyes. This reaction may be modified so as to give a very vivid demonstration of the action of inhibitors. By addition of a small quantity of hydroquinone to the alcoholic solution of safranin, we note that on exposure to ozone no chemiluminescence results, the dyestuff is not oxidised, but after a minute or two the hydroquinone is completely oxidised, and the brilliant green glow of the dyestuff undergoing oxidation spreads over the bulb.

We have already indicated the possible connection between chemiluminescence and reversed photochemical action postulating in both cases the generation of an excited molecule formed in the former by chemical and in the latter by radiant processes. This analogy may be pursued somewhat further by a consideration of the mechanism of photochemical sensitisation and its reversal. In cases of photochemical sensitisation a molecule excited by the absorption of radiation conveys by collision part or all of its energy to a molecule of another species, which subsequently undergoes chemical reaction. The beautiful experiments of Frank and Cario in forming chemically reactive hydrogen by sensitisation with mercury vapour excited by the line  $\lambda 2537 \text{ \AA}^\circ$  may be cited as a case of photochemical sensitisation. A similar complimentary reaction in chemiluminescence has been observed by Kautsky, who showed that the energy liberated as chemiluminescence in the oxidation of the suboxide of silicon, siloxene, could be transferred to certain dyestuffs, causing them to become excited and undergoing fluorescence. Only those dyestuffs such as fluorescein and eosine, which are absorbed by the crystals of the siloxene, can be made to fluoresce, an indication that the energy necessary for excitation of the dyestuff molecule must be transmitted by collision from one of the surface molecules of the solid reacting siloxene which in turn must pass through the stage of an excited molecule during oxidation. The experiments initiated by Haber and Zisch on the interaction of the alkali metals with halogens and halides have more recently been re-examined by numerous investigators, notably Kondratjew, Ljallikoff and Polanyi; these all exhibit beautiful chemiluminescent effects. The interaction of sodium and iodine vapour, and of potassium and iodine demonstrate the various phenomena to be observed in these reactions, and analysis of the radiation emitted as well as of the distribution on the tube walls of the salt formed, gives us a clue to the mechanism of the reaction. In the interaction of sodium vapour and iodine we may compute the thermal changes accompanying all the possible reactions.

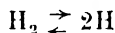


It is observed that the D line is only emitted corresponding to a chain luminescent emission of 48.3 cal. Of the four reactions listed above only two are accompanied with sufficient energy for the liberation of the D line, viz. (2) and (3). A further observation that the chemiluminescence possesses in this case a negative temperature coefficient suggests that only one of these reactions, viz.  $\text{Na}_2 + \text{I} = \text{NaI} + \text{Na}$  is responsible for the chemiluminescence observed in the gas phase, and that neither (2) nor (4) take place in the gas phase except in a reaction more involved than a bimolecular one. The tube walls catalyse both reactions (2) and (4) effectively. The surface catalysed reaction is clearly observed in the union of potassium and iodine for the reaction (3) does not occur to an appreciable extent when sodium is replaced by potassium on account of the low concentration of diatomic potassium molecules in the vapour of the element.

The bulk of chemiluminescent processes can accordingly be represented as



Chemiluminescent methods may be employed not only to identify, as noted above, the nature of the molecular processes involved in a chemical reaction, but also to affix within certain limits at least the energy of dissociation of certain gases. Thus, simple dissociation process



in reality must be much more complicated in operation than the unimolecular bimolecular dynamic equilibrium postulated by this equation given in the text-books. Whilst the efficiency of collision in causing reaction of complex molecules such as  $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$  is usually high that of atomic recombination is very low, and if we regard a pair of normal atoms in close proximity to one another as the extreme case of dissociation, the absence of an electric moment in the system forbids the quantised emission of radiation. Thus reactions such as  $2\text{H} \rightarrow \text{H}_2$ ,  $2\text{Br} \rightarrow \text{Br}_2$ , only occur in presence of a third body or a surface, and the energy of combination transmitted to the third body is frequently emitted as chemiluminescence, a phenomenon readily observed with atomic hydrogen. The energy of combination of atomic hydrogen is found to be sufficiently great to excite the OH molecule to emission but not the mercury line  $\lambda 2537 \text{ \AA}^\circ$  in mercury atoms: this places the energy of dissociation of hydrogen between 94,000 and 112,000 cal. per gm. molec.<sup>10</sup>. Atomic hydrogen readily prepared by Wood's method is a convenient source of many chemiluminescent experiments. The afterglow of a number of gases,

notably oxygen, nitrogen dioxide and nitrogen, when excited by the electric discharge may all be regarded as chemiluminescent reactions in that the gases possess enhanced chemical reactivity in the glowing state. The glow of nitrogen dioxide and nitric oxide, and the after-glow of Lord Rayleigh's active nitrogen are particularly brilliant, but the chemical processes involved are at present obscure. It seems at least definitely established that active nitrogen contains at least two chemically reactive species both atoms and excited molecules. The cohesion of solid surfaces may be regarded as a species of chemical reaction in the solid state, and several of these reactions are found to be chemiluminescent, although frequently classified as tribo or crystaloluminescent reactions, the crystallisation of arsenious oxide, sugar, exemplify this class of reaction.

Other quasi-chemical reactions which are luminescent include the fluorescence and phosphorescence excited in various substances, especially in solid solutions by electron bombardment, some of the effects produced by the bombardment of minerals, such as kunzite, by high speed electrons, are particularly brilliant. Finally, we may observe the chemiluminescence obtained with certain bacteria such as *B. fluorescens*, and the reaction between luciferin and luciferase, the basis of biological light.

[E. K. R.]

Friday, March 1, 1929.

HIS GRACE THE DUKE OF NORTHUMBERLAND, K.G. C.B.E. M.V.O.,  
President, in the Chair.

SIR ROBERT ROBERTSON, K.B.E. M.A. F.R.S.,  
Secretary, Royal Institution.

### Infra-Red Spectra.

#### HISTORICAL.

IN the year 1800 the elder Herschell, by placing a thermometer in the region lying beyond the visible red of the solar spectrum, gave the first experimental proof of the existence of radiation there by observing a rise in temperature of the instrument, and his son in 1840 described the existence of emission bands in the same region as shown by a discontinuous evaporation of alcohol from blackened paper placed in the same region.

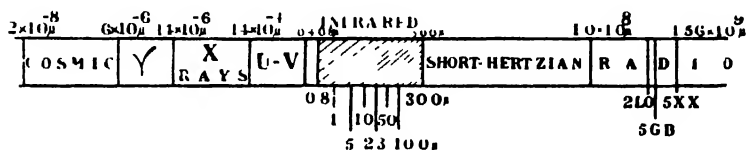
To illustrate action beyond the visible red of the spectrum the following experiment was made. As it was impractical to use the sun's spectrum, the beam from an arc lamp was dispersed by means of a large rock-salt prism, giving the usual spectrum visible to the eye. A card on which a phosphorescent powder (calcium sulphide with nickel as impurity) was first caused to glow brightly by subjection outside the theatre to ultra-violet light from a mercury lamp and then placed in the spectrum, when the existence of radiation beyond the visible was shown by the quenching of the phosphorescence for some distance past the red.

This region of the spectrum attracted much interest from the middle of last century and onwards, when instruments of increasingly refined character were evolved to detect and measure effects of emission and absorption of radiation there. Thus photography was tried, and Abney succeeded in penetrating the region for a short distance, which has not been exceeded by more recent workers employing special sensitisers for their plates. Langley with the bolometer, Boys with the radiomicrometer, and Coblentz with the thermopile, succeeding in measuring quantitatively radiation in the infra-red; the last two instruments are the principal ones employed to-day in that region which lies nearest to the visible. Still farther out measurement of the energy in the beam dispersed by means of reflexion from the polished surface of crystals gave important results

in the hands of Rubens and his colleagues, while within the last year Raman, by an entirely different technique, to be mentioned later, has indicated how infra-red radiations can be deduced from spectroscopic measurements in the visible spectrum.

### ELECTROMAGNETIC WAVES.

The relationship of the infra-red region to other parts of the spectrum was illustrated by a diagram simplified from that prepared by Dr. F. E. Smith (see "Phases of Science," 1925), in which the whole range of electromagnetic waves from  $\gamma$  rays to the longest radio waves, and only completed in recent years, is set forth. On this diagram were indicated the respective lengths of the waves from



Velocity = 30,000,000,000 cms. per sec. = 186,000 miles per sec.

crest to crest in each region; the cosmic rays of Millikan, supposed by him to proceed from the birth of atoms such as helium, oxygen, silicon and iron, in the profound depths of space at the lowest extremes of temperature and pressure, of a wave-length of about  $2 \times 10^{-8} \mu$  ( $\mu = 0.001$  mm.); the highly penetrative  $\gamma$  rays about  $4 \times 10^{-6} \mu$ , which accompany radioactive change; the X-rays about  $1.5 \times 10^{-5} \mu$ , also penetrative of matter on account of their short wave-lengths; the ultra-violet rays to about  $0.4 \mu$ , which promote many chemical reactions; the visible spectrum, from about  $0.4$  to  $0.8 \mu$ ; infra-red rays from  $0.8 \mu$  to about  $23 \mu$ . (the near infra-red) or to  $300 \mu$  (the far infra-red); heat rays and short Hertzian rays to  $1 \times 10^4 \mu$ ; and then the rays used for wireless whose length may be measured in miles, 5XX for example being 1560 metres, or about a mile long. It is a characteristic of all these waves, from the shortest to the longest, that they are propagated at the same speed, the speed of visible light, or 186,000 miles a second.

The clue to the properties of these waves was found by Faraday when he discovered rotation of the plane of polarisation of light in the magnetic field, a discovery of which Tyndall said "I would liken it to the Weisshorn among mountains, high, beautiful and alone." This in turn was translated by Clerk-Maxwell into the succinct notation of mathematics, and it formed the basis of his electromagnetic theory, the foundation of modern electromechanics. Since then the likeness in character of these electromagnetic waves has



been shown by their being capable of dispersion, interference, resonance, and by many other physical properties.

As to the effects of the radiations in different parts of the spectrum it may be said that, whereas in the shorter wave-length regions comprising the  $\gamma$ , X-rays and visible spectrum, these are mostly electronic, in the infra-red region the transitions are caused by changes in the oscillatory states of the atoms in the molecule or in the rotational states of the molecule itself.

#### QUANTITATIVE MEASUREMENT OF INFRA-RED BANDS.

Dispersion by means of a grating having been referred to, a modern infra-red spectrometer of Hilger was then described as to its respective parts, the source of radiation (a Nernst filament), the slits, the reflecting mirrors, the dispersing prism (of quartz up to  $3\mu$ , of fluorite up to  $8\mu$ , of rock salt up to  $17\mu$ , or of sylvin up to  $23\mu$ ), and the thermopile. Special reference was made to the thermopile, composed of bismuth-silver couples used in conjunction with a galvanometer for measuring the energy passing through the instrument. Its sensitiveness was illustrated by allowing a little compressed air to enter a sealed bell-jar containing the instrument, when, by adiabatic compression of the air, the heat generated was registered by movement of a spot of light from a Moll galvanometer.

An experiment was then performed to illustrate the method of mapping an absorption band, ammonia being the gas employed, and the arrangements simplified from those described in Proc. Roy. Soc. A, **120**, 128 (1928). Two tubes were so arranged that they could alternately be thrown into the optical path between the source of radiation and the spectrometer, one tube being empty while the other contained  $\text{NH}_3$  gas. The energy passing through the respective tubes was measured by a galvanometer which threw a spot of light on a large scale on the wall of the theatre. At  $1.8\mu$  the difference between the throw of empty and gas tubes was small, but this difference increased up to  $2.2\mu$ , and then decreased. These differences were noted and then plotted against wave-length on co-ordinates marked out on the blackboard, when a distinct band due to absorption by  $\text{NH}_3$  appeared in this region. Examples of absorption bands (*l.c.* pp. 168 and 175) were then shown as slides.

#### OSCILLATION BANDS.

Bands due to both oscillation of the atoms in the molecule and rotation of the molecule itself are found in the infra-red spectrum. Oscillation bands were shown by Drude, from the phenomenon of dispersion in crystals, to be necessarily present having wave-lengths such as occur in this region of the spectrum, if certain smaller charged particles (electrons) are concerned in the ultra-violet region. As the effect is one of resonance, the atoms in a molecule respond in

their vibration to radiation possessing some particular frequency, and this was illustrated by a model in which a ball suspended on a spring from the end of a light rod supported on two nodes was made to perform vertical oscillations, whereupon a ball similarly suspended at the other end of the rod picked them up and vibrated vertically in phase with the former ball. The electronic linking between the atoms prevents their oscillation being truly sinusoidal; harmonics may therefore be expected and are in fact found. This was illustrated by a table from the work of the author and Dr. Fox on  $\text{NH}_3$ ,  $\text{PH}_3$  and  $\text{AsH}_3$  (*l.c.*, p. 190).

### ROTATION BANDS.

Molecules also undergo rotation, and this effect is reflected in their infra-red spectra. It was pointed out that the main bands were due to oscillation, but that in addition the rotation of the molecule also produces bands, of a simple character, in the far infra-red, but in the near infra-red as fringes superimposed on the oscillation bands. Rayleigh, assuming on the basis of classical mechanics a Maxwellian distribution of velocities, in 1892 showed that an oscillator emitting and absorbing at a frequency  $\nu_0$  due to its oscillations alone would, when rotating about an axis perpendicular to its line of vibration with a frequency  $\nu_r$ , emit and absorb at the new frequencies  $\nu_0 + \nu_r$  and  $\nu_0 - \nu_r$ . This seemed at first to meet the case, as in some of the early bands such as those of Burmeister two broad areas occurred which the Maxwellian distribution of rotational velocities would require. In 1911, however, Nernst concluded that rotation must also be quantised, and in 1912 Bjerrum and E. v. Bahr resolved a band of  $\text{HCl}$  into a series of small bands, which they ascribed to the effects of rotation of the molecule. This band has been better resolved by Innes and others, and from the spacing of the fringes the diameter of the molecule of  $\text{HCl}$  has been calculated. Sommerfeld, applying the principle of Bohr, showed that the equal spacing of the fringes was best explained by quantising the moment of momentum, so that each quantum jump represents a change in the moment of momentum. If the moment of momentum  $J\omega$  is taken as a whole multiple of

$$\frac{h}{2\pi}, \quad J\omega = \frac{m}{2\pi} \frac{h}{\pi} \text{ and } E_{\text{rot}} = \frac{h^2}{8\pi^2 J} m^2$$

by the Bohr-Einstein conception

$$h\nu = E - E_1 = \frac{h^2}{8\pi^2 J} \left[ m^2 - (m+1)^2 \right] = \frac{h^2}{8\pi^2 J} (2m-1),$$

whence the space difference is  $\frac{h}{4\pi^2 J}$ , a result in accordance with facts. It will be seen that by putting the spacing difference

$\Delta \nu = \frac{h}{4\pi^2 J}$ , the moment of inertia of the molecule ( $J$ ) can be calculated, and, from the moment of inertia, given the masses of the vibrating atoms, the length of the molecule.

#### INFORMATION GIVEN BY INFRA-RED SPECTRA.

In the first place we get the frequency of oscillation of the atoms within the molecule, and the frequency of rotation of the molecule itself. These have been shown for a simple molecule such as that of HCl.

But, in addition, with more complicated molecules, it is possible to construct models by taking into consideration the presence of absorption bands and assuming a law of force between the atoms in the molecule. Thus Hund for  $\text{NH}_3$  considers that it has a tetrahedral structure, and this is probably also the case with the analogous  $\text{PH}_3$  and  $\text{AsH}_3$ . With these gases have been found at least three sequences of bands in each, corresponding with three degrees of freedom of oscillation, one of the sequences in each gas having five or six harmonics. In this sequence the frequency of vibration gets slower as the weight of the atoms  $\text{N} \rightarrow \text{P} \rightarrow \text{As}$  increases in the three gases.

It is interesting from the chemical point of view to see if any of these degrees of freedom correspond to the chemical bonds of the chemists, and some hint of this is obtained in one case at least. Thus by progressively substituting the H in  $\text{NH}_3$  by  $\text{CH}_3$  a certain band—the first harmonic of the main sequence mentioned above—disappears from the spectrum after the last H has been substituted, so this degree of freedom of oscillation has been identified as connected with the chemical bond  $\text{N}-\text{H}$ .

Again, as regards rotation we have found two moments of inertia in  $\text{NH}_3$  of which one can be attributed to rotation round the median line and the other round the centre of mass at right angles to the median line. Calculation of the length of the molecule, as above described, gives a value similar to, although somewhat smaller than, that obtained by Rankine from measurements of viscosity of this gas.

By the comparison of spectra of related compounds, as for example in the case of hydrocarbons, definite bands have been attributed to certain groups or radicals. In the case of solids certain groupings such as  $\text{NH}_4^+$  or  $\text{CO}_3^-$  have similarly been identified in the spectrum of salts.

In the hands of Coblentz infra-red data and technique have been used to determine the quantity of radiation from the sun, stars and planets, and he has also deduced the temperatures which prevail in these bodies, and even the differences in radiation from the hemispheres of Mars.

The knowledge of the infra-red spectrum of water vapour and of  $\text{CO}_2$  is of importance in considering the nature and quality of energy reaching us from the sun, and only recently Dr. G. C. Simpson, by making use of the absorption coefficients of water and carbon dioxide in the infra-red, has deduced that an increase in solar radiation would result in increased cloud and precipitation and even in the apparent paradox of an ice age. Further, Paschen's determination of the emission and absorption bands of these gases is fundamental in questions relating to combustion.

#### FUTURE WORK IN THE INFRA-RED REGION.

Such are some of the results that spring from the consideration of infra-red spectra.

On the more theoretical side it has thrown light on and given support to the quantum theory. It has passed into the hands of the still more modern exponents of the wave mechanics and found to be in accord with their predictions, as for example in connexion with the assumption of half quantum numbers. This is a field in which its usefulness is only beginning.

Only last year Prof. Raman, of Calcutta, by imposing monochromatic radiation from a mercury lamp on gases and liquids, observed spectroscopically in the scattered light not only the original line but also others at frequency differences which he finds are equal to frequencies in the infra-red at which bands characteristic of the gas or liquid were known. This brilliant experimental confirmation of the quantum theory may prove of the highest importance from a theoretical point of view when it comes to be explained why in the Raman effect not all the bands found in the infra-red by the usual means appear, and why others appear to be disclosed only by the Raman effect.

Like the X-rays it deals with the structure of the molecule, but while X-rays reveal the molecule in its static condition and are especially applicable to solids, infra-red spectra reveal the dynamic characteristics of the molecule in gases, liquids, and to a restricted degree in solids. In the future it will undoubtedly be used to a greater extent in the determination of the nature of chemical linkages, and generally for a solution of problems of chemical constitution.

As Garner and his school have shown, important deductions can be made as to the rôle of infra-red radiation in combustion, as, for example, in the effect of water, when it is present, in carrying off the energy of radiation produced when CO combines with oxygen, and as the bulk of the radiation from flames is in the invisible part of the spectrum and mainly in the infra-red, there is here a wide field of work in clearing up the mystery of flame, and the same is true

as regards the phenomena of explosion of both gaseous and solid explosives.

It is to be regretted, however, that more work is not being done in this country in the exploration of this region. It is true that the technique is difficult, and there have been several investigations reported the accuracy of which leaves a good deal to be desired. Most of the work up till now has been done in Germany and in the United States, little so far having come from our Universities, with the exception of Cambridge, where there is an embryonic school.

The subject is perhaps scarcely one suitable for a young graduate to acquire the technique and embody a year's work in a thesis for some degree, but one for a more permanent staff; and I should like to make a plea for its greater consideration in this country as a field of experiment and study likely to assist in the solution of many physical and chemical problems, which in due course will have its reflexion in the domain of technical application.

Sir J. J. Thomson has given us the electron, Rutherford the proton with its planetary electrons and the structure of the proton, the Braggs have elucidated the structure of many molecular fabrics, but the molecule as a dynamical entity has been comparatively neglected. For it is in the infra-red region of the spectrum that this behaviour can best be studied. In this aspect the problem is a physical one for the most part; the technique is difficult, but likely to be productive of much that is important in our conception of the structure of matter. It is for this reason that one would like to see in this country a strong school arise having as its object the study of the dynamical behaviour of the atoms in the molecule and of the molecule itself.

[R. R.]

Friday, March 22, 1929.

SIR JAMES CRICHTON-BROWNE, J.P. M.D. LL.D. F.R.S.,  
Vice-President, in the Chair.

SIR ERNEST RUTHERFORD, O.M. LL.D. Pres.R.S. M.R.I.,  
Professor of Natural Philosophy, R.I., and Cavendish Professor of  
Experimental Physics, University of Cambridge.

### Penetrating Radiations.

[ABSTRACT.]

In recent years there has been a rapid growth in our knowledge of new types of electromagnetic radiations of very short wave lengths which are able to penetrate great thicknesses of matter before they are absorbed. The discovery of X-rays, which correspond to light waves of very short wave length, opened up a new field of study, and this was further widened by the discovery that radium and other radioactive bodies emitted radiations of the same type, but of a far greater power of penetration. A still further extension of our ideas has come from the proof that there exists in our atmosphere a type of ultra-penetrating rays, often called the cosmic rays, of about 100 times the penetrating power of gamma rays. The frequency of vibration of these cosmic rays is from 100 to 1000 million times greater than that of ordinary light.

The main factors which control the absorption of these radiations are now well understood. For ordinary X-rays the quantum of radiation in passing through the atoms of matter occasionally collides, or rather interacts, with one of the component electrons, and the whole wave-energy of the quantum is given to the electron, which is set in rapid motion and ionizes the matter in its path. The chance of such a conversion of the energy of the radiation, called the photo-electric effect, increases rapidly with the weight of the atom, and falls off markedly as the frequency of the radiation is raised. It is for this reason that, weight for weight, heavy elements absorb X-rays much more easily than light elements.

Another process, called scattering, which leads to loss of energy from the radiation is also always present. The effect of this is small for ordinary X-rays, but becomes predominant for very high frequency rays, and indeed controls the absorption. In this scattering process, called the Compton effect, there is a peculiar type of interaction between the quantum and the electron which differs markedly

from the photo-electric effect. The radiation is scattered, and at the same time the electron is set in motion. The scattered radiation is degraded in frequency in amount depending on the angle of scattering. In very penetrating rays the average frequency of the scattered wave is reduced to about one-half for each scattering collision, and about half the energy on the average is given to the recoil electron. Consequently when a very penetrating radiation passes through matter recoil electrons of high speed and degraded radiations are always present.

A number of experiments were shown to illustrate the laws of absorption of penetrating radiations of the X-ray and  $\gamma$ -ray types. A new method devised by Professor H. Geiger for detecting and counting the individual recoil electrons produced by the penetrating radiations in our atmosphere was shown in operation.

The experimental information is at present too scanty to fix with certainty the origin and nature of these extraordinarily penetrating rays. It has been suggested that they come from outer space, and represent radiations which arise in the destruction or creation of atoms. The energy of the quantum in the most penetrating radiation measured by Millikan is of the order of 1000 million volts. It may prove significant that radiation of this energy may be expected to arise if the proton can be converted into radiation by a single catastrophic process. Some time ago Jeans suggested that the transformation of protons and electrons into the energy of radiation appeared to be necessary in order to account for the long lives of the hot stars.

[E. R.]

Friday, May 31, 1929.

MAJOR CHARLES E. S. PHILLIPS, O.B.E. F.Inst.P.,  
Secretary and Vice-President, in the Chair.

F. N. DA C. ANDRADE, D.Sc. Ph.D. M.R.I.  
Quain Professor of Physics, University of London.

### The Air-Pump, Past and Present.

To create and conserve nothing in a jar, to make but one molecule grow where ten million grew before, may seem to the uninitiated a paltry and destructive aim, but it has nevertheless long been the task of countless men of learning, and this search after vacuity has led to some of the most important discoveries in science. On the one hand, the great advances which atomic physics has made within our lifetime—the isolation of the electron; the discovery of the X-rays with which our illustrious director has illuminated the dark places in the structure of solids; the achievements of spectroscopy, of radio-activity, and every other branch of modern physical science—are inseparably bound up with the creation of a vacuum; on the other hand, the speedy evacuation of vessels is a fundamental feature of that great branch of the electrical industry which we may comprehend in the term “lamp manufacture,” the lamps in question being not only those which give out visible electromagnetic radiation, but also the thermionic valves which take part in the emission of long waves, and the X-ray tubes which generate the very short waves. Members of the Royal Institution and their friends have often seen here various beautiful experiments carried out with evacuated tubes of different forms; to-night I hope that you will bear with me if I bring before you certain aspects of the indispensable tool by which the evacuation is carried out: the air-pump, to use the time-honoured name, although as often as not its task is to deal with gases and vapours other than air. The general principles of many modern types of pump is so well foreshadowed in the early history of the instrument that I shall venture to begin with the birth of the instrument, and then try to trace down to the present day the general principles as they have developed.

The first experiments on vacua were made by Otto von Guericke, whose earliest attempts were certainly carried out before 1652, possibly in the 1630's. He began by filling a cask with water, and



then pumping out the water with a brass fire-squirt adapted for the purpose. The attempt naturally did not succeed, the air rushing in through the crevices of the cask. Having failed to overcome this difficulty by making a smaller cask, which was put inside the larger one, the inter-space being filled with water which might reasonably be supposed to leak into the pumped-out cask more slowly than air, Guericke prepared a copper sphere, filled with water, which was likewise pumped out with the squirt. While the pumping was in progress the sphere collapsed "with a very great noise, to the terror of all, like a cloth that is crumpled in the hand." In these early attempts we already have the fundamental principle of a great number of air-pumps down to modern times, namely to fill the space to be evacuated with some substance, liquid or solid, and then to withdraw that substance. Guericke himself next proceeded to make a true air-pump with a solid, instead of a liquid, piston. This first effective pump is not illustrated in Guericke's own book *De Vacuo Spatio*, which was not published until 1672, but by his permission an account of it, with an illustration, was given by Gaspar Schott in his *Mechanica Hydraulico-Pneumatica*, 1657 (see Fig. 1). The cylinder of the pump was arranged at a slope, so that the lower end could be immersed in water, to seal the joint with the receiver (a method commonly used in those days, anticipating our modern mercury seals), and was provided with an internal valve at the receiver end, and one valve opening into the atmosphere placed, not very advantageously, about half-way up the cylinder. It was with such a pump that Guericke performed the first experiments on the properties of vacuous spaces, in particular the famous experiment of the Magdeburg hemispheres, and many others designed to exhibit the pressure of the atmosphere, which Guericke clearly understood.

Our Robert Boyle first heard of the air-pump through Schott's book, and set about making his much improved "engine," in constructing which he was materially aided by the no less famous Robert Hooke. The action of this pump was controlled by a tap between the pump-cylinder and the receiver, and by a plug valve, opened and closed by hand, controlling a port connecting the bore of the cylinder with the outside air. With this pump, and with an improved model which he made shortly after, Boyle carried out a wonderful variety of experiments, both physical and biological. He showed, among other things, that sound was not propagated, and that a candle went out, in an evacuated vessel, while the action of a magnet and of a spring were unaffected by the evacuation. He also demonstrated with various animals—cats, shrew-mice, frogs and snails—the troubles of living creatures in very attenuated air, and further, even made an apparatus for distillation in vacuo. Meanwhile various other celebrated men, including Huygens and Guericke himself, were producing pumps with various new features of construction. A great step forward was made by Boyle, aided this time by the ingenious

and inventive Papin, when about 1680 he made a two-cylinder pump, the two pistons being connected by a cord passing over a pulley. With the single-cylinder pump the effort of withdrawing the piston becomes very great as exhaustion proceeds; with the two-cylinder pump one piston helps to raise the other.

The achievements in the way of piston-pumps of the preceding fifty years or so are embodied and extended in the famous two-cylinder pump of Hawksbee, described by him in 1709. The pistons

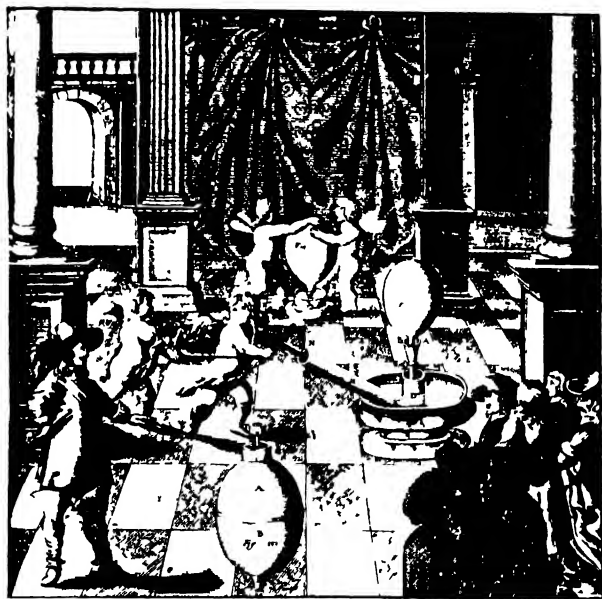


FIG. 1.—GUERICKE'S FIRST AIR-PUMP.

This pump is not figured by Guericke in *De Vacuo Spatio*, 1672, but by Father Schott, in his *Mechanica Hydraulico-Pneumatica*, 1657, which gives the first published account of the Magdeburg experiments.

are raised and lowered by a pinion-wheel engaging in two racks. With this pump Hawksbee performed the first experiments on the discharge of electricity in vacuo, the ancestors of so famous a line. Another experiment he performed, which I now repeat for you, has been the subject of a series of researches by the present Lord Rayleigh, researches which he has described at the Institution.\* A

\* Proceedings of the Royal Institution, vol. xxiv, p. 471, 1925.

bottle containing a little oil in which pieces of phosphorus have been allowed to stand is shaken so that the oil wets the whole interior, and placed under a receiver, which is then exhausted. As exhaustion proceeds the whole bottle suddenly becomes highly luminous, the luminosity diminishing again when the pressure becomes very low. As we are dealing with the pump itself I must not devote more time to these early experiments, but I may say that in the early years of the eighteenth century the pump was so far perfected that it became a popular means of entertainment, and Mr. Vream, for instance, in his little book published in 1717, gives no less than fifty experiments which may be performed by its aid.

The type of piston-pump built by Hawksbee continued without essential change until late in the nineteenth century, when great improvements were embodied in the so-called oil-pumps invented by Fleuss, and christened by him "Geryk pumps." A layer of oil, of very low vapour pressure, placed on top of the piston, does away with any dead space, while the closing of the cylinder at the top avoids any atmospheric pressure on top of the piston, so that even with a single cylinder it requires no effort to pump at low pressure. The cylinder is divided into two parts, the piston rod passing through the dividing diaphragm, leakage being avoided by a layer of oil on top. When the piston is raised it lifts a valve in the diaphragm, and the oil layer on top of the piston, having completely expelled all air, passes partly through the valve; when the piston is lowered oil follows it until the valve closes. In the most recent types of pump, which are run at a high speed, the pressure attained is actually below the vapour-pressure of the oil used in the pump. How this can be possible will be clearer when we have considered the modern vapour-stream pumps.

Another early method of obtaining a vacuum, figured in the *Saggi di Naturali Esperienze*, published by the Accademia del Cimento in 1666, is to fill a long tube, the closed end of which widens out into a vessel of some capacity, with mercury, and then to invert it, so that a Torricellian vacuum is produced, in which various experiments can be produced. This we may call the method of the liquid piston. Its modern descendants are the various forms of Toeppler pump in general use round about the end of the last century. In these pumps a Torricellian vacuum is repeatedly produced by the raising of a vessel of mercury, and this vacuum is automatically connected with the receiver every time the vessel is lowered.

A very great advance in the technique of obtaining a vacuum was made by Gaede in 1905, when he produced his rotary mercury pump. A drum of special construction is divided into compartments which, by rotation, are successively filled with mercury, and then emptied, each compartment being connected in turn to the receiver as the emptying takes place. This is a clever adaptation of the principle of the liquid piston, which immediately obtained great



FIG 2.—RAMELLI'S ROTARY PUMP

From Ramelli's *Diuerse et Artificiose Machine* 1598. The pump consists of a revolving drum with radially sliding vanes mounted eccentrically in a cylindrical case, and closely resembles in design the type of modern American rotary air pump shown in Fig 3.

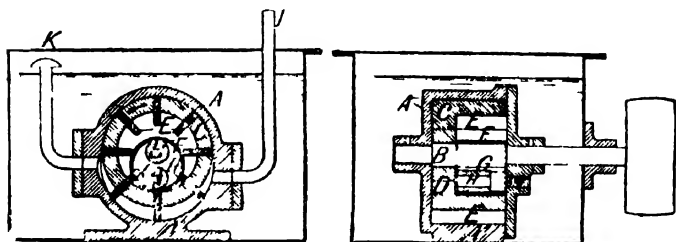


FIG 3.—MODERN TRIMOUNT ROTARY PUMP, for comparison with Ramelli's pump

popularity in all laboratories. It is to be noted that, in order that the drum may not be of unwieldy size, it is necessary to reduce the pressure in the casing which encloses the drum, so that the level of mercury inside and outside the drum may not exceed a centimetre or so. The Gaede rotary pump, therefore, had to be used in conjunction with a preliminary pump, or fore-pump (German *Vorpumpe*).

The ingenuity of the sixteenth and seventeenth centuries found expression in many peculiar forms of pumps designed to handle water and other liquids, especially in a variety of pumps in which the liquid was swept up by scrapers or vanes making close contact with the interior wall of a casing. Examples due to Ramelli and to Prince Rupert are shown in the slides (see Figs. 2 and 4). With the increasing perfection of engineering practice pumps have in modern times been made on exactly the same principle to deal with gases (see Figs. 3 and 5). Gaede's so-called box-pump (*Kapselpumpe*) follows closely the design of Prince Rupert's "water-bolt." It can easily produce a soft X-ray vacuum. In another very popular type of vane pump, the "Hyvac," the vane is in the wall of the casing, and presses on the solid drum which rotates eccentrically, the point of contact with the casing continually changing. By the courtesy of Messrs. Edwards, the English agents for this pump, I am able to show you the extraordinary rapidity with which the large pattern pump will produce an X-ray vacuum in a large vessel.

All the pumps which we have so far considered are based on purely mechanical principles, and for their understanding it is quite sufficient to consider a gas as an elastic fluid, continuous in structure. The molecular character of the gas is in no way involved, and, as we have seen, modern pumps of the type in question are merely direct descendants of pumps devised long before this molecular character was realised. It is to emphasise this point that I have adopted the historical aspect. We now turn, however, to the new types of pump, designed within the past twenty years, which are based upon what may be generally called molecular principles, and demand for their understanding a study of the physical nature of a gas. In particular the properties of gases at low pressure are involved, for the pumps in question are, so to speak, only finishing pumps, and do not come into action until a rough pump has already prepared the way for them.

According to the kinetic theory a gas consists of molecules, which may be considered as little spheres, or, more generally, as little bodies of a more or less marked degree of symmetry, about a hundred-millionth of an inch long, rushing about in all directions and frequently colliding with one another and with the walls of the vessel. The collisions with the walls produce the pressure. The molecules move with a very high velocity, some hundreds of yards per second for gases at ordinary temperature, and this high velocity, deduced from elementary considerations, was a point of difficulty in

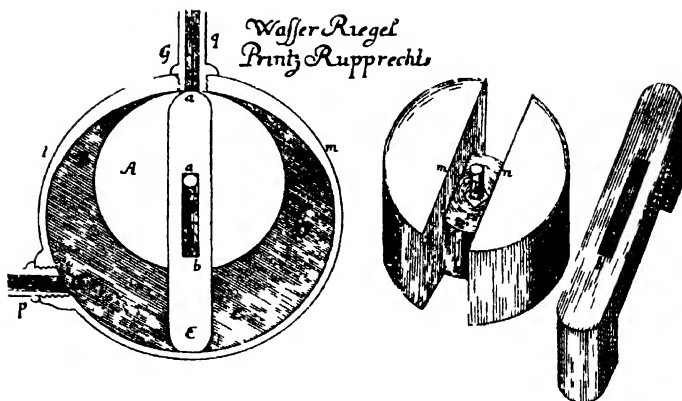


FIG 4—EARLY ROTARY PUMP

Prince Rupert's "water bolt" designed in the middle of the seventeenth century as a water pump. The picture is from Leupold, *Theatrum Hydraulicarum* 1724. Compare with the design of that type of modern pump called the *Kapselpumpe* by Gaede.

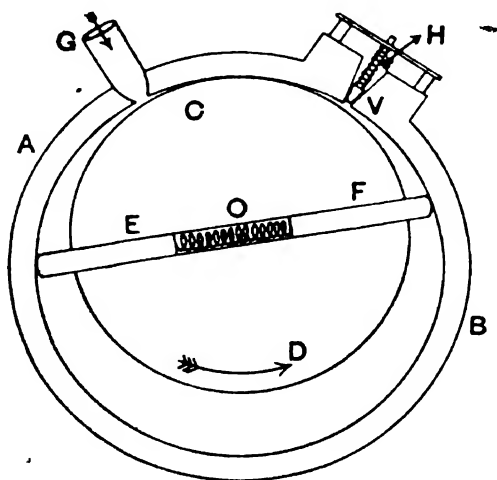


FIG 5—MODERN ROTARY AIR-PUMP

For comparison with above Gaede's *Kapselpumpe*

the early days of the theory, critics objecting that such speeds would imply very rapid diffusion, so that, for instance, the vapour of any odorous liquid should be detected by its smell at the furthest parts of a room as soon as the bottle is opened. Such criticism leaves out of account the frequent collisions, which make the path of an individual molecule a zigzag with frequent turns back on itself. The average distance between collisions is called the mean free path, and is an essential factor in all questions of diffusion and of viscous forces. It is about a hundred-thousandth of a centimetre for air at ordinary pressure, and is, to a first approximation, independent of the temperature. It varies, with a given gas, inversely as the pressure, so that at low pressures it becomes quite large: in air at a pressure of 1 microbar it is 10 cm., and at a pressure of .01 microbar, easily attained with modern technique, it is 10 metres.

If we consider the passage of a gas through a tube of any kind, a change in the laws governing the movement begins to manifest itself when the pressure becomes low enough for the mean free path to be about equal to the linear dimension of the cross section of the tube. The physical reason of this is clear: at higher pressures most of the collisions are between molecules, collisions with the walls being comparatively infrequent; at very low pressure collisions with the walls are common compared with those between molecules, and dictate the nature of the bulk movement of the gas. Knudsen, who studied the flow of gases through tubes at very low pressure, found that his results could be explained on the supposition that the molecules which struck the walls did not bounce off at the reflecting angle, like tennis balls from a smooth floor, but came off in random directions, like tennis balls thrown into a crowd, where they are caught and thrown up again at hazard. The gas behaves as if momentarily condensed on the wall, and then re-evaporated. He worked out the consequences of such behaviour, and deduced laws which he found to agree closely with experiment. If the quantity  $Q$  of gas issuing be measured by the volume multiplied by the pressure at which it issues, then

$$Q = pv = \frac{4}{3} \sqrt{2} \pi (p_2 - p_1) \frac{r^3}{l} \frac{1}{\sqrt{\rho}} t$$

where  $\rho$  is the density of the gas at unit pressure;  $p_1$  and  $p_2$  are the pressures at the two ends of the tube respectively;  $r$  is the radius and  $l$  the length of the tube;  $t$  is the time. This formula shows that a gas at low pressure will take a surprisingly long time to pass through quite a wide tube into a perfectly exhausted vessel. For instance, suppose a volume of 2 litres, containing air at 15° and at a pressure of 10 microbars, connected by a tube 50 centimetres long and 5 millimetres in diameter to a second vessel in which a pump maintains a pressure of only .1 microbar. It will take 5 minutes

for the pressure in the first vessel to fall to  $\cdot 2$  microbar. Many physicists who are familiar with this speak, however, as if the resistance to flow at low pressure were *greater* than that which we should anticipate if the ordinary law of flow which holds for higher pressure, viz.,

$$Q = pv = \frac{\eta (p_2 - p_1)}{8 \eta l} p r^4,$$

with constant coefficient of viscosity  $\eta$ , held down to very low pressures. This is, however, incorrect, the resistance at such low pressures being less than if the normal laws of viscosity were valid. For instance, if we take oxygen at such a pressure that the mean free path equals the radius  $r$  of the tube, we find that Knudsen's formula indicates rather more than four times as much gas passing through under a given pressure difference as would issue if the ordinary viscosity formula were applicable. The reason that, even so, wide tubes offer such a large resistance to the flow of gases at low pressure, is that the driving difference of pressure is very small. It is therefore necessary with all modern vacuum pumps to have very wide connecting tubes, made as short as possible, and very wide bore taps, if exhaustion is to proceed efficiently.

I can show you the slow passage of low pressure gas with the help of this tube, some 10 metres long and about 7 mm. internal diameter. At each end the tube opens out into a vacuum tube of ordinary type with its pair of electrodes, so that the pressure prevailing can be indicated by the type of discharge. One end of the tube goes to a high vacuum pump, the other end is drawn out and sealed. The tube is pumped out, and a small hole is then pierced, by means of a spark, in the drawn-out end. The entering air at once indicates its presence in the first vacuum tube, but many seconds elapse before it appears in the second, as evidenced by the discharge. The interval represents the time required for the air to traverse the tube.

Considerations of the behaviour of gases at low pressure led Gaede in 1912 to design a new type of pump, termed by him a molecular pump. Since the molecules behave as if condensed on the surface, and then quickly re-evaporated, if we move the surface rapidly we communicate a common velocity component to all molecules. If, then, part of the walls of a tube could by some means be kept in steady motion in the direction of the length of the tube a difference of pressure would be maintained between the two ends of the tube, the tendency of the gas to flow under the difference of pressure being counteracted by the drift imposed on the molecules. Calculation shows that with a given gas the *ratio* of the pressures at the two ends is fixed by the speed of the walls and the length of the tube. If the ordinary laws of viscosity were valid at these low pressures the *difference* of pressure would be fixed in this way.



Clearly the ratio of pressure also depends upon the ratio of the speed of the gas molecule to the speed with which the walls move, so that at a given temperature this pressure ratio is much less for hydrogen than for a heavier gas.

In Gaede's pump the walls of the supposititious tube, which has just been discussed, are constituted by grooves cut in a drum which can be set in very rapid rotation. The drum fits closely into a housing from which a tongue protrudes into each groove, dividing the groove into a low pressure side, where the walls are running from the tongue, and a high pressure side, where the walls are approaching the tongue. The high pressure side of one groove is connected to the low pressure side of the next groove, so that we have virtually several pumps in series. A preliminary pressure of a fraction of a millimetre of mercury (say  $\cdot 1$  mm.) is necessary to ensure the efficient working of this type of pump, but with such conditions a very low vacuum can be rapidly attained. A great advantage of pumps of this type is that they deal with condensable vapour as readily as with gases.

Another form of molecular pump has been recently designed by Holweck. In this pump a spiral groove is cut in the casing, and the drum has an unbroken cylindrical surface. The depth of the groove is tapered so as to allow for the decrease of mean free path with increasing pressure. By the courtesy of Messrs. Hilger, the English agents, I am able to show the rapidity with which a large sized Holweck pump can evacuate a vessel of some litres capacity down to a hard X-ray vacuum. No precautions have been taken to exclude water vapour.

We now turn to another type of pump which has come into great general use in the last few years. As a preliminary let us consider the influence of a volatile liquid on a vacuum, in particular the question of obtaining a high vacuum in a vessel connected to which by a wide tube is a second vessel containing a liquid.

A celebrated German text-book of physics, published in 1906 says, for instance, "If a receiver containing a little gas is in connection with a pump that contains mercury, the pressure of the gas cannot be less than  $\cdot 0013$  mm. (the vapour pressure of mercury), and if there is mercury vapour in the receiver the total pressure cannot be less than  $\cdot 0013$  mm. of mercury." This sounds reasonable, and is indeed true so long as everything is at rest, and the problem is a statical one. It need not be true, however, if the vapours are streaming. We can, for instance, actually connect a receiver to another vessel containing boiling mercury, and yet have a very low pressure in it. To do this we put a liquid air trap in between; the pressure in the trap is very low indeed, and there is a continuous stream of mercury vapour into it; the vapour condenses and the pressure in the receiver remains exceedingly low. To show this I have two tubes containing electrodes, so that the pressure can be

tested by applying a high potential in the usual way ; the two tubes are connected by a wide tube so diverted in the middle that it can be immersed in liquid air. The one tube is connected with a small vessel containing mercury. First of all the whole system is pumped out until the discharge of the same type in both tubes indicates a hard X-ray vacuum. The liquid air vessel is then put in position and the mercury heated by a flame. The discharge in the tube connected directly to the mercury vessel takes on the bright green character indicative of mercury vapour at a considerable pressure ; in the other tube, on the far side of the trap, the hard X-ray vacuum is maintained.

Gaede obtained some very interesting results by connecting a vessel containing a little air with a vessel of heated mercury, with an ice-cooled trap between the two vessels. If the total pressure of gas and mercury vapour were the same in both vessels, then, since there is only air in one, when the mercury is heated sufficiently to give this pressure, there should be no air in the other. However, it was found that air diffuses into the mercury vapour space against the current of vapour. The laws of diffusion are somewhat complicated, but Gaede worked out the case in detail, everything being at low pressure, and his results led him to devise his mercury vapour pump.

The principle is to let the gas diffuse into a rapid stream of mercury vapour which carries it away to a place where it can be removed by a rough pump. The vapour stream is produced by strongly heating liquid mercury : vapour which diffuses into the receiver space is condensed. Although the fore-vacuum is necessarily at a higher pressure than the receiver gas cannot get back against the stream of mercury vapour. The pump will only work well at low pressure, for unless the mean free path is long the diffusion process does not become really operative. To render the diffusion effective Gaede used a slit, which diminishes the counter-current of mercury vapour. This case can be worked out mathematically, and it can be shown that diffusion is most effective when the width of the slit is equal to the mean free path of the gas. If the slit is too wide the density of the mercury vapour is too great, and the "brush" action of the slit loses its sharpness ; if it is too narrow not enough gas molecules diffuse through. Similarly, if the vapour pressure is too high the counter-current is too vigorous ; if it is too low the stream is not fast enough. I can show you this experimentally. You will observe that if I heat the mercury in this pump too vigorously the action of the pump becomes less efficient, as witnessed by the discharge in the tube which is being evacuated ; if I remove the flame altogether, so that the pump cools, the action improves again.

A better arrangement of the vapour stream was devised by Langmuir. In his type of pump the vapour issues through a tube, which is surrounded by a wider tube, the walls of which are water-

cooled. The tube to the receiver enters the outer tube at a point in the rear of the vapour jet. If the pressure is so low that the mean free path of the vapour is greater than the distance between the tubes, the molecules cannot diffuse back against the gas stream, but strike the wall and condense. It is true that a much lower temperature than the boiling point of mercury is needed for condensation at such low pressures, but with tap-water cooling the condensation is fairly effective. The importance of condensation is clear, and Langmuir called his pump a condensation pump, but the gas enters the vapour stream by diffusion just as in Gaede's pump. Both the original Gaede pump and Langmuir's pump are really diffusion-condensation pumps.

As diffusion is more effective with hydrogen than with other gases, say carbon dioxide, the diffusion pump should be more effective in evacuating hydrogen than with any other gas; on the other hand, I have pointed out that the molecular pump is least effective with hydrogen. To show this experimentally I have two exactly similar discharge tubes into which I introduce a mixture of hydrogen and carbon dioxide, the tubes being connected together so that the mixture is identical in each. I now close the tap between the two tubes and let a molecular pump evacuate the one, a vapour stream pump the other, for a short time. The former shows at once a pink discharge, indicating that the remaining mixture is strong in hydrogen; the latter shows a bluish discharge, indicating relative richness in carbon dioxide.

The different types of diffusion pump all need a good preliminary vacuum, as they cannot hold up against more than a slight difference of pressure without gas coming back against the vapour stream. A fore-pump producing something between a tenth and a hundredth of a millimetre of mercury should be employed. However, at higher pressures, where the diffusion effect is small, we can use the steam-injector principle, for in a jet of fast-moving comparatively dense vapour there will be a diminution of pressure corresponding to the kinetic energy of the accelerated vapour. The surrounding gas will flow in as a whole under the difference of total pressure, not partial pressure. This principle has been used for the creation of a fore vacuum by a vapour stream. In Gaede's three-stage steel mercury-vapour pump, for instance, which has great speed of pumping, there is an injection stage working at comparatively high pressure, and a diffusion stage for the lowest pressure, while in between there is a stage of mixed action.

Mercury is not the only liquid which is suitable for use in a vapour pump. Quite recently Mr. Burch, by a process of distillation in vacuo, has obtained an oil the vapour pressure of which at ordinary room temperatures is extraordinarily low. This oil can be used effectively as the working fluid in pumps. Another liquid which can be used is normal butyl phthalate. As, to the best of my

knowledge, this substance has never been employed in England for this purpose, I will now use it in a small glass pump to produce an X-ray vacuum.

While we have now briefly reviewed the chief types of vacuum pumps, properly so called, it must be remembered that other processes are widely used, especially in industrial laboratories, for producing high vacua. Solid surfaces in general exercise a marked condensing action on gases, and absorb on themselves thin layers of gases at temperatures and pressures under which the substance is gaseous in bulk. Consideration of these surface actions lie outside the scope of this discourse, as do the methods of combining the residual gases chemically with a substance which deposits on the walls of the glass, by the use of the so-called "getters." We may, however, with reference to the part which the walls of the vessel play in these processes, refer to these methods as *mural* methods. If we are allowed to do this we may alliteratively divide the methods of producing high vacua into *mechanical*, described in the first part of this discourse; *molecular*, including in this term both what is ordinarily called the molecular pump and also the vapour stream pumps, since they are based upon molecular theory; and *mural*. The action of the first is perfectly understood; the action of the second is largely understood, but more difficult; the third method, though widely applied, is theoretically still very obscure in many cases.

Finally, it may be mentioned that while pressures as low as a ten-thousand-millionth of atmospheric pressure can be certainly produced in the laboratory, even at this pressure more than a thousand million molecules are present in every cubic centimetre. We are still very far from being able to produce the kind of vacuum that exists in outer space.

[E. N. DA C. A.]

Friday, January 24, 1930.

WILLIAM HENRY ECCLES, D.Sc. F.R.S., Manager and Vice-President,  
in the Chair.

SIR WILLIAM BRAGG, K.B.E. D.Sc. F.R.S. M.R.I.  
Fullerian Professor of Chemistry.

### Cellulose in the Light of the X-Rays.

ONE of the most fascinating features that emerge during the closer study of natural constructions is surely the extended use of certain atoms, certain molecules, and certain ways of combining molecules; while other atoms, molecules, and combinations are but seldom employed. Thus, for example, half the world of which we have knowledge is made of oxygen: silicon is used to the extent of 27 per cent., aluminium 8 per cent., iron and a few others make up most of the remainder, and some eighty or more of the 92 kinds of atoms cannot muster 2 per cent. between them. The seas that cover the larger part of the earth's surface give the water molecule  $H_2O$  easy precedence over all others. In the rocks, the oxygen atoms govern the structure: the recent work on the silicates by W. L. Bragg and his collaborators shows us that we may regard the great bulk of the earth's crust as a piling together of bulky oxygen atoms cemented by atoms of other kinds such as silicon, aluminium, iron, or magnesium. Sometimes the piling is of the simplest character, and seems to depend for the most part on considerations of space to be occupied. Sometimes, as in quartz, more complicated structures are framed in order to satisfy the directional qualities of the mutual attractions of silicon and oxygen.

If we take special note of the elements of living structure, the extraordinary predominance of the carbon atom at once attracts attention. Though the mass of carbon in the world is only about a fortieth of one per cent. of the whole, its importance to life is extreme.

Two forms of molecular constitution are outstanding: the long chain of carbon atoms which is the basis of so many substances, fats, oils, paraffins, and so on, and the benzene ring in which six carbon atoms are tied together strongly into hexagonal form. A very large proportion of organic chemistry deals with the properties of these two forms of molecules and their derivatives; they are of the greatest importance in regard both to biochemistry and to the chemistry of industry.

## CELLULOSE AND FIBRES.

Cellulose is the fundamental molecular combination occurring in vegetable growth. One has but to remember that forests and shrubs and grasses and plants of all kinds are mainly composed of cellulose to realise the strangeness of such a particular selection. What is there in the cellulose molecule or combination of molecules that its responsibility should be so great? It is pre-eminently the molecule of growth in the vegetable world. It is found in the animal world also. It must be a molecule by the aid of which purpose and direction can be worked out. A mass of cellulose as it occurs in a plant cannot be of equal properties in all directions, for growth has to take place along definite lines. With one or two stray exceptions, such as asbestos, the bulk of inorganic substances do not display that curious feature which we describe in a word as "fibre."

Cellulose is a fibrous material, and its molecule or molecular combination must somehow give it this fundamental character. The fibrous character of the stem and leaves of plants is their most obvious characteristic: the marked quality of direction is at the basis of their manner of growth and their constructional possibilities. These qualities, moreover, we use for our own purposes. We spin the natural fibres of cotton and hemp, ramie, jute, and the like, forming threads and ropes which have the special quality of standing strain in one direction. We weave cotton goods; and we use the comminuted cellulose to make paper. In these cases the fibres are distributed in one plane in more than one direction, and so form sheets that stand two-dimensional strain. Of late years the cellulose, specially treated in various ways, is drawn out into threads of artificial silk, or rayon. This fibrous quality is therefore essential not only to Nature's employment to cellulose, but also to the use that we make of it. We should like to know exactly what cellulose is, and what there is in the curious structure that justifies this extensive use.

## CHEMISTRY OF CELLULOSE.

The main attack upon the question has been made by the chemists, who have found it a simple matter to analyse cellulose into its constituent atoms: it may be described as a multiple of  $C_6H_{10}O_5$ . But of course this description is quite insufficient to explain its properties: there are, in fact, several other substances of the same composition, such as starch, glycogen, dextrin. The distinctive properties of cellulose must depend on how these twenty-one atoms are arranged with respect to one another. We must therefore endeavour to discover the design. It would be quite out of place to attempt a description here of the chemist's attack upon the problem of position. We have already heard, at the Royal Institution, a general

account of the atomic positions in the sugar molecule from Sir James Irvine, who has himself been a pioneer in this field. Cellulose is closely allied to the sugars; indeed their basic features are the same. A brief description of some of the chemical results will be quite sufficient for our purpose.

It is certain that the six carbon atoms are connected in a chain. But the chain is not to be thought of as drawn out in a straight line. The chemist writes a formula of a straight line character, when he wishes merely to show which atom is attached to which, but his meaning goes no further. Fig. 1 shows the usual method of writing the formula for glucose, of which the  $C_6H_{10}O_5$  group is the anhydrous form.

Each carbon atom is attached to four other atoms: the positions of the hydrogens and the OH groups, right or left of the carbons, have a meaning in that if any pair is inverted the character of the substance changes. The most curious feature of the diagram is the connexion of the first and the fifth carbon atoms through an oxygen.

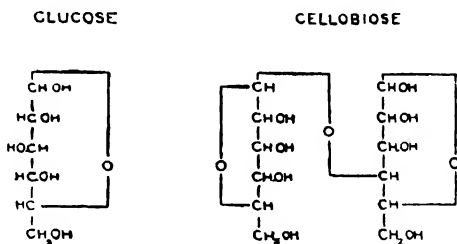


FIG. 1.

Possibly the diagram is wrong in that it should be the fourth that is joined to the first. The latter view was favoured for many years, but later researches, especially by Haworth, make the 1:5 junction the more probable, and we will adopt it provisionally.

Clearly, when we come to think of this set of atoms as a group in space, we must make arrangements for the oxygen at the side of the diagram to get into contact with the two atoms to which the formula attaches it. Getting into contact means that the centre to centre distance between two atoms is a quantity which under similar conditions may be considered to be fairly constant. It would be impossible to think of an oxygen touching the first and last of five carbons in a straight line. The chain must be bent round until contact is possible, and at once we have the idea of a six-atom ring, five carbons and one oxygen.

There is no doubt that this ring is the basic element of all living plants and of numbers of those substances which can be derived or made from plant materials. The fact stirs the imagination and the





tion. It is further held that by tacking on a third ring with a similar oxygen linkage cellobiose may be extended to form cellotriose, which consists of three rings; and that, finally, by the continued addition of ring, up to an indefinite number, we have the essential structure of cellulose. The actual arrangement in space is probably as represented in Fig. 2, but this diagram contains some information which only X-rays could supply. We had therefore better leave the construction at this point and consider the X-ray evidence.

### EVIDENCE OF X-RAY METHODS.

Let us remember that the new method of X-ray analysis derives its power from its capacity to detect any regularity of arrangement of atoms or molecules. To such dispositions it is very sensitive: it can record a perfect array of a few hundred molecules or so, or an imperfect array if the number is greater.

We have seen that there must be in cellulose some directed quality, if it is to play so important a part in growth as it appears to do. Of course, it may be said that direction is possibly attached as a property to some other constituent of the plant, the identity of which is yet unknown. But, on one hand, cellulose is common to all plants, and their most prominent content; on the other, it turns out, as will appear, that it is easy to understand how cellulose can have the quality that we look for. Now we cannot imagine how direction is to be obtained without regularity of arrangement. There must be a pattern, involving the constant repetition of some form of grouping, which we might expect to be related to the line of growth. We might then look at once for some such effect when an X-ray is sent through a fibre of cotton or ramie or hemp, as we have become accustomed to find when X-rays act on a photographic plate after traversing a crystal. A crystal is merely a crowd of atoms in regular array.

When the experiment is made, the effect is found at once. Moreover it is a kind that we recognise as indicative of fibrous nature. Let us look at this point a little more closely.

When a pencil of homogeneous X-rays passes through a crystal which is made to revolve about an axis, one set of crystal planes after another comes to its proper angle for reflection, and the reflected ray leaves the crystal in a direction inclined to the primary pencil at twice the reflecting angle. We must remember that all the lattice points in the crystal, that is to say, points representing all the units of pattern, can be looked on in an infinite number of ways as lying on sets of parallel, equi-distant planes. The proper angle for reflection  $\theta$  is connected with the wave-length ( $\lambda$ ) of the rays and the spacing ( $d$ ) of the planes by the law  $n\lambda = 2d \sin \theta$ ,  $n$  being any integer.

A photographic plate may be placed to receive the various reflected rays; and if both rotation axis and plate are perpendicular to

the primary pencil, a symmetrical figure is formed on the plate. An example is given in Fig. 3. The crystal was in this case asparagine, which is a derivative of one of the constituents of wool. The weight of the crystal was of the order of a milligram.

From the positions of the spots and their intensities the X-ray methods draw information respecting the crystal structure. This is clearly a matter of calculation, based partly on geometry and partly on physical theories as to the reflection process. We do not stop to

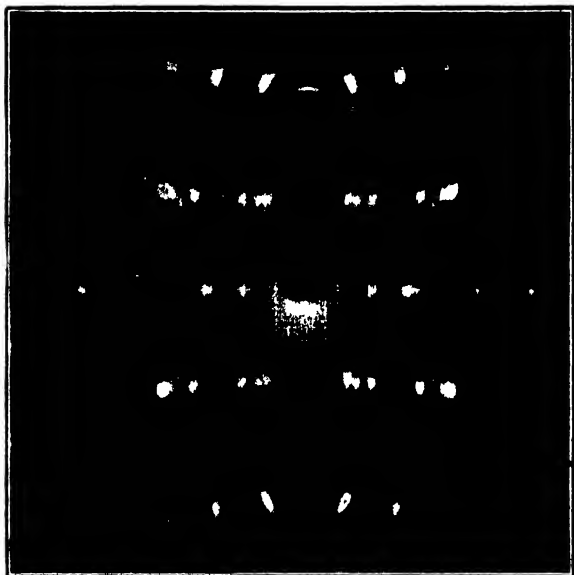


FIG. 3. —Asparagine. X-ray diagram, obtained by W. H. George using the "rotation" method. The X-rays are monochromatic, and the crystal is rotated during the exposure. The network at the back of this diagram is placed there for convenience of interpretation.

consider the details. The work of interpretation is by no means easy at all points; but some results can be obtained at once and accurately, others are more difficult and less certain.

The clear separation of the spots on the asparagine photograph and their arrangement on a few well-marked lines show that the axis of rotation has coincided with an important direction in the crystal; that is to say, a line which passes through many lattice points to the unit of length, and is the intersection of a number of important sets of planes. The lattice points lying on the axis are of necessity

equally spaced along it; this must be so in a crystal. The magnitude of this spacing is readily obtained from the photograph. The spots obviously lie on a set of hyperbolæ. If  $v_n$  denotes the distance of the vertex of the  $n$ th hyperbola from the horizontal line, which is called the equator, and if  $D$  is the distance from the crystal to the photographic plate, the spacing in question is equal to  $(\lambda \operatorname{cosec} \theta)/n$  where  $\tan \theta = v_n/D$ . The proof of this rule is to be found in books on this subject. Unless the spots are very hazy, this determination can be made with, at the very least, an accuracy of one or two per cent.

Obviously, if a crystal were made to revolve about three different axes (not coplanar), we should in a similar way find the periodicities in three corresponding directions in space and so determine the form of the crystal lattice.

#### X-RAY DIAGRAM OF CELLULOSE.

Now if we take some cellulose fibre, such as ramie, and place it so that a fine pencil of homogeneous rays passes through it, afterwards falling on a photographic plate as in the experiment just described, we find that a spot design appears on the plate of exactly the same character as that of the asparagine photograph. It is clear, therefore, that the fibre is in some respects crystalline. There is, however, one significant peculiarity in the manner of obtaining the ramie photograph. It is not necessary to rotate the substance as in the case of the asparagine. The explanation is that the ramie contains not one crystal but many crystals which have in common one important direction; it must be important because the photograph has clear lines. Otherwise the crystals may have any disposition about this line as axis, so that the diagram is like that which a single crystal gives when it is made to rotate.

It will be observed that the ramie photograph (Fig. 4) is not so clear as the other. That is mainly due to the incompleteness of the array of the crystals with respect to each other.

Suppose that the disarray were complete, as it would be if the fibrous material were so pounded or otherwise treated that the crystals pointed all ways. There could then be no particular directions on the photograph; no vertical or horizontal lines of symmetry. There could only be a set of rings, as if the fibre photograph were spun rapidly in its own plane about its centre. An example of such a photograph is given in Fig. 5; the material is cystine, one of the constituents of wool. It is due to W. T. Astbury, of the Textile Research Department at the University of Leeds.

When the spots in the photograph are sharp, we conclude that the crystals are well oriented in respect to one direction, the fibre direction. When there is no orientation at all, the result is as in

Fig. 5. Every stage between is possible; with a small departure from orientation the spots merely begin to spread along the circles on which they lie.

Some of the blurring is due, however, to the smallness of the crystals. The X-ray action is of the nature of a diffraction, and it is well-known that sharp images denote the combined action of many regularly arranged objects and vice versa. It is even possible to estimate roughly the number of diffracting centres in the crystal from the spreading of the spot. This has been done by H. Mark, whose work on the whole subject is of first importance.

If now we measure the distances of the vertices of the hyperbolæ



FIG. 4.—X-ray photograph of ramie fibre.

from the equator in this ramie photograph, we can, as already explained, find the length of the periodicity along the rotation axis. It comes out to be  $10\cdot3$  A. ( $1$  A. =  $10^{-8}$  cm.).

Summing up, we know that :

(1) Cellulose contains crystals which may be invisible in the microscope but are clearly indicated by the X-rays; they are usually termed crystallites.

(2) These crystallites are partly oriented, having one direction in common, more or less.

(3) In each crystallite there is a periodicity in this special direction of  $10\cdot3$  A. This is often called the "identity period."

It may not be safe to say that the whole of the cellulose is

composed of crystallites, but there is a strong temptation to assume that this is so. Cellulose is a multiple, as regards content, of the unit  $C_6H_{10}O_5$ , as we have seen reason to suppose that this unit forms a ring which is the basis of the structure. The X-rays do not suggest the presence of a second structure, having any real difference from the first: and we suppose, therefore, that the ring structure pervades the mass. When the X-ray methods become more reliable in the matter of measuring the intensities of the reflection due to a given

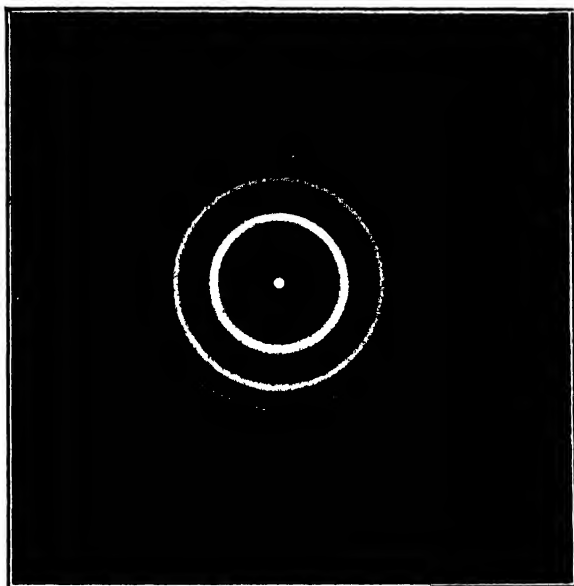


FIG. 5 — Cystine. This kind of diagram, due to W. T. Astbury, is typical of a substance consisting of a multitude of very small crystals, not arranged with respect to each other.

weight of the substance, in comparison with other substances of similar and known structure, we shall be able no doubt to answer this question conclusively.

#### COMPARISON OF THE CHEMICAL AND X-RAY ANALYSES.

We now return to the results of the chemical examination of cellulose and ask how our new results harmonise therewith. As regards the first two deductions stated above, there can of course be no contradiction: we have simply obtained some additional information on the matter of structure. But the third deduction is of rather

a different nature. If chemistry has suggested a special arrangement of the atoms, it must show a reason for the periodicity that has been discovered. Now the X-rays have shown us that atoms of carbon and oxygen, when built into the regular structure of crystals, can be said to have dimensions. They do not behave so simply as to warrant our thinking of them as hard spheres. But when the state of combination of two atoms is known, the distance apart of their centres can be stated within limits so close as to give a determining value to estimates of structure.

We know that two carbon atoms bound together in that strong fashion, which is sometimes described as due to the exercise of principle valencies, and is found in diamond, graphite, benzene, hydrocarbons, and the like, are at a distance of very nearly 1.5 Å. from one another, centre to centre. We are not quite so sure of the value of the similar distance in the case of oxygen and carbon. But from parallel cases in calcite and elsewhere we can safely assume that it is about 1.2 Å. In Fig. 2, due to Mark, an attempt is made to apply these known distances to the determination of the dimensions of the cellobiose double ring. There is naturally some uncertainty about it because the form of the ring is not yet known accurately. Moreover, the way in which the oxygen bridge is fitted in, while by no means devised *ad hoc*, can only be assumed from analogy with somewhat similar cases in other crystals.

The length of the double ring comes out at 10.3 Å., agreeing with the X-ray results. Notwithstanding all its possibilities of error, such a coincidence is most striking. It certainly supports excellently the idea that cellulose is essentially a long chain compound in which the glucose rings form the successive links, being attached to one another by oxygen bridges as shown in Fig. 2. According to Haworth ("Constitution of Sugars," p. 84) the unit that is constantly repeated is formed of two rings or links, not of one, which means that the links differ from one another alternately. A difference of this kind is shown in Mark's figure: the oxygen bridges lie, it will be observed, alternately on one side and on the other of the principle plane of the molecule. There is an imperfect repetition of the pattern of each link, and a perfect repetition at each second link. It is known that such a condition should manifest itself in the X-ray diagram by the weakness of the spots in the first, third, and odd numbered hyperbolæ as compared with the strength of the spots in the even numbered. The effect may wear off in the hyperbolæ of high number. The weakness of the first cellulose hyperbola as compared with the second is very obvious.

Thus the X-ray evidence is certainly, so far, in favour of the conception of cellulose as formed of chains of glucose rings. Throughout the whole length of the chain the bonds are of the strong type such as are found in diamond. The conception has been put forward before (Herzog, *Zeit. ang. Chem.*, **34**, 385; 1921. Polanyi,

*Naturwiss.*, 1921, 288), though by no means accepted. It is described, for example, in Haworth's "Sugars." The American botanist Sponsler, who has also used X-ray methods, has maintained it ("Colloid Symposium Monograph," 1926). In particular, H. Mark has argued strongly in favour of it, and has supported his views by much experimental research. Nevertheless, there are cellulose chemists to whom the idea does not appeal: Trogus and Hess, for example, have argued against it quite recently.

If we try to estimate the value of such evidence as this, and of much more that will presently be considered, we must recognise that it is not fully decisive. On one hand, there are many factors which are not fully understood; on the other, the X-ray analysis is clearly far from its full development and does not yet handle its problems with the assurance of long experience. But even now the X-ray evidence has a distinct value: it may be expected to be worth much more in the future. In this particular case it is satisfactory to prove a periodicity which a very interesting and promising theory of cellulose would lead us to expect.

#### THE UNIT OF PATTERN OF CELLULOSE.

The diagram has obviously more to tell us than the value of the one periodicity we have been considering. The positions of the separate spots have information to give which goes far to determine the form and dimensions of the unit of pattern. Suppose the unit to be represented by the rhomboidal cell in Fig. 6. The implication

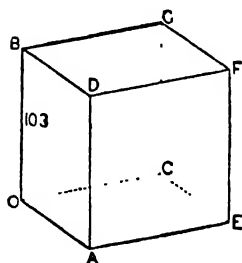


FIG. 6.

of the "cell" is that if we moved our point of view in the crystal from *O* to *A* or to *B* or to *C*, we should not be able to detect the change. Suppose that *OB* is the periodicity we have found, which we distinguish by writing 10·3 alongside. All the other dimensions of the cell have yet to be found.

Every spot on the equator is made by a set of planes to which *OB* is parallel. For example, the set of planes of which the planes *OBDA* and *GFE* are consecutive members, contribute one spot to the equator row, and the position of the spot on the diagram gives us the perpendicular

distance between the two faces mentioned. So also for the pair *OBGC* and *ADFE*. We may pick out two spots on the equator and decide, as we can with certain limitations which need not be discussed here, that we will make the planes to which these spots belong the faces of the unit cell. But the diagram does not tell us directly what angle these faces make with each other. If we

had a single crystal instead of a multitude we should have no difficulty, because we should make a variety of diagrams by revolving the crystal about at least two other directions, such as  $OA$  and  $OC$ . It is this lack of the single crystal that most contributes to the difficulty of our task.

Nevertheless, we are not without means which will guide us indirectly, if less certainly, to a conclusion. To begin with, the general appearance of the diagram considered in comparison with others of like origin suggests strongly that the crystal is nearly if not quite monoclinic. In other words, the direction of periodicity  $OA$  and  $OC$  are nearly if not quite perpendicular to  $OB$ . We may safely assume for the present that they are so. For brevity's sake I do not argue this out in full. If this is assumed, we have but one unknown left, namely, the angle between  $OA$  and  $OC$ . To find it we have the perpendiculars from  $A$  on  $OC$  and from  $C$  on  $OA$ . Also a definite assumption will carry with it the positions of all the other spots on the diagram, and though this is not so liberal in fresh information as it sounds, yet on the whole the determination of the angle is restricted to one or two very distinct possibilities.

Much argument has been spent on the final choice. It appears that all the details of the diagram are well satisfied if it is assumed that  $OA = 8.35 \text{ \AA}$ ,  $OC = 7.9 \text{ \AA}$ , and the angle  $COA = 84^\circ$  nearly. We have already determined  $OB$  to be  $10.3$  (Mark and Meyer, *Zeit. Phys. Chem.*, B. 2, 115; Andress, *Zeit. Phys. Chem.*, B. 2, 380).

An approximate knowledge of the specific gravity of cellulose is enough to show that this cell contains four of the  $(C_6H_{10}O_5)$  groups.

Our picture is now taking shape. We picture these long chains as arranged parallel to  $OB$  (Fig. 6). If the axis of one chain lies along  $OB$ , the axes of exactly similar chains lie along  $AD$ ,  $EF$ , and  $CG$ . Such an arrangement places the matter of two glucose rings within the six walls of the cell, thus accounting for two out of the four rings. Here calculations based on the relative intensities of various spots come to our aid, and in a manner which can be found in accounts of X-ray methods, tell us that there is a chain in the middle of the cell, passing approximately through the centres of the faces  $OAEC$  and  $BDFG$ . This accounts for the other two rings.

### THE CRYSTALLITES.

We must think, therefore, of the crystallite as composed of these long chains laid side by side like a bundle of sticks. This prompts us to consider next the manner in which the sticks are held together.

Now there is an obvious difference between the forces that bind together the links in each chain and those that bind together the chains themselves. The former are relatively very strong, all of them being of the nature of those that are found in diamond. But



the latter are due to the mutual action of carbon atoms the primary valencies of which are satisfied by attachments of hydrogens and of hydroxyl groups. They are more of the nature of the forces that bind molecule to molecule in organic crystals like naphthalene. When naphthalene melts or sublims, its molecules are separated and these secondary valencies are snapped. But the work to be done is very small in comparison with that which is required to snap the primary valencies in the molecule itself. There are no hydroxyl groups in naphthalene, so that the secondary forces are not so large as those we may expect to find in our present case. But still there must be a very great difference between the forces within the chain and those from chain to chain.

We find internal evidence in the structure of our model which is entirely in sympathy with this view. While the centre to centre

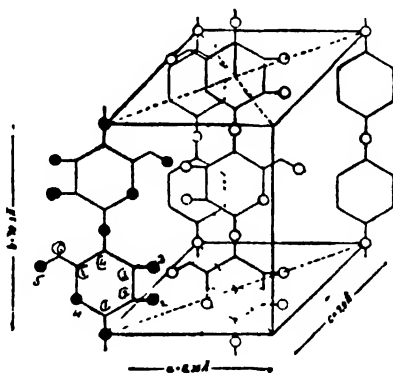


FIG. 7.—Skeleton diagram showing the relative positions of the chains. (From Mark and Meyer, *Zeit. phys. Chem. B.* 2, 122; 1929.)

distance of carbon atoms bound by primary valencies is nearly  $1.5 \text{ \AA}$ ., the distance of closest approach of carbon atoms belonging to different molecules is about  $3.5 \text{ \AA}$ . In graphite, for example, the layers are separated by a distance of  $3.41 \text{ \AA}$ . In naphthalene the corresponding distance is about  $3.5 \text{ \AA}$ .; in the fatty acids it is the same. If we consider the cellulose model, we see that some such distance must be assumed here also. Otherwise, the chains would not come into contact with each other; they would not fill up the volume. For example, the model shows the planes of the ring lying mainly in the  $ab$  and parallel planes, as in Fig. 7, due to Mark and Meyer (*Zeit. phys. Chem.*, B. 2, 122; 1929). The reflection from this set of planes is by far the strongest on the diagram, which is indeed a very important guide to the construction of the model. The distance from plane to plane is  $3.95 \text{ \AA}$ ., which fits in very well with hypothesis.

## TEMPERATURE EFFECTS.

A certain measure of confirmation comes from a different quarter. The coefficient of expansion of diamond with temperature is exceedingly small. In the case of graphite it is very small in the plane of the sheets, but many times greater at right angles thereto. (Backhurst, *Proc. Roy. Soc.*, 102, 340; 1922). In other words, the sheets do not stretch as the temperature rises, but draw apart from each other.

It is to be remembered that a comparison of X-ray diagrams at different temperatures shows the expansion coefficients in every direction in a crystal. This is possible even when the crystal is microscopically invisible, though the accuracy is not so great as when we have a single perfect crystal that can be handled.

The observations on diamond and graphite suggest strongly that the strong carbon bonds in diamond and graphite stretch or contract very little with changes of temperature, while in the case of the weak



Fig. 8.—X-ray photographs of a paraffin,  $C_{18}H_{38}$ , at the ordinary temperature (A), and at the temperature of liquid air (B). (Dr. A. Muller.) The lines in the centre are due to the various orders of reflection by the long spacing, which is actually the length of the carbon chain. These are in the same positions in the two photographs. But certain lines farther out are due to the sideways spacings of the chains, and these are considerably shifted by the change in temperature.

bond in graphite there is a very appreciable alteration in the centre to centre distance.

The point is further illustrated by an effective experiment due to Dr. Muller. A comparison of the two photographs in Fig. 8 shows that temperature affects the length of a carbon chain far less than the distance that separates the chains from one another.

No doubt the changes in form which a crystal experiences when the temperature is varied are often complicated and are difficult to interpret. But in these simple cases it seems clear that we are observing a difference in the reaction of primary and secondary valencies.

We might certainly expect very little change in the dimensions along the cellulose chain when the temperature is lowered to that of liquid air. This is exactly what Mark and Meyer have found (*Zeit. phys. Chem.*, B, 2, 127). But there is a considerable change in other directions

## MERCERISATION.

The process known as mercerisation, so very interesting from the scientific point of view, and so important industrially, produces notable changes in the X-ray diagram. Yet so many of the original features remain that the new structure is obviously to be regarded as a modification of the old. Most important is the fact that there is no change in the dimensions of the separate links of the chain. Andress (*Zeit. phys. Chem.* B 4, 190) has shown that the new diagram can be fully explained if the sideways relations of the chains with respect to each other are somewhat varied, in the manner depicted in Figs. 9 and 10. The new arrangement is regarded as that of the stable form of the crystal, the older as the metastable.

The permanence of the identity period along the chain, and therefore of the chain itself, survives not only a physical alteration such as mercerisation, but also various chemical changes. For ex-

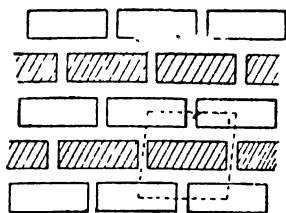


FIG. 9.—General disposition of the cellulose chains, looking along the  $c$  axis.

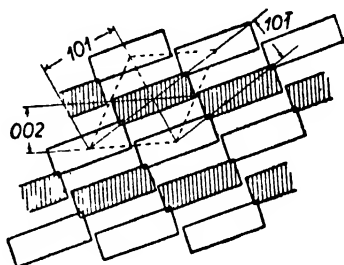


FIG. 10.—General disposition of the chains in mercerised cellulose, looking along the  $c$  axis.

ample, there are forms of trimethylcellulose, of acetyl-cellulose, and of nitrocellulose, which are crystalline, are of the same general form as cellulose itself, and have the same periodicity of  $10\cdot3$  in the fibre direction. In other directions there are great changes; clearly the introduction of new atomic groups between the chains must push them apart, though there may be no change in the chains lengthways. When by chemical means the stranger atoms have been taken away again, the original X-ray diagram of cellulose is restored; except that in some cases, depending on the nature of the treatment, the diagram of the recovered material is that of mercerised cellulose.

There are, however, other examples of cellulose derivatives which show a more radical change as the result of chemical action. Another form of nitrocellulose shows, according to Mark, an identity period of 25 A.; and 15 A. has been found in an acetylcellulose and a cuproamine cellulose.

So, in general, the chain seems to retain its nature even when subjected to wide changes of temperature and to many chemical processes. All this is in entire accord with the conception of the chain of glucose rings tied together through its whole length by strong bonds resembling those of diamond : a conception encouraged by the studies of the sugar chemists and now supported by the X-ray evidence. By sideways bonds the chains are tied together into bundles or micelles, and when the chains are long enough these sideways bonds, though individually far weaker than the others and more susceptible to physical and chemical action, will be strong enough to hold the bundle together as a definite element in the structure of the cellulose. The process of the stretching and recovery from strain which fibres show in different degrees and ways owe their many complications to the varied possibilities of gradual alterations in the alinement of the micelles, of their sliding past each other, of their partial recoveries, of their hysteresis, of their final partings when the strain is too great. But these properties of fibre are fully treated in other places.

In fine, we have a striking and in some respects a very simple picture. A particular form of atomic combination has been chosen by Nature to be the basis of all plant structure, and in its essential structure it already embodies the fibre principle. The X-ray analysis at least supports and gives some precision to views as to structure which have already been suggested. There are great possibilities of improvement in the X-ray methods ; and it may well be that before long their pronouncements will be much more definite.

[W. H. B.]

Friday, January 31, 1930.

GEORGE C. SIMPSON, C.B. C.B.E. D.Sc. F.R.S., Manager and  
Vice-President, in the Chair.

LORD RAYLEIGH, Sc.D. F.R.S. M.R.I.

### Iridescent Colour in Nature.

[ABSTRACT.]

THE colours of insects are of two distinct classes. Some of them are due to pigmentary substances, just as are the colours of oil or water-colour pictures, or dyed fabrics. For instance, an ordinary English tortoiseshell butterfly owes its red colour to this cause, and accordingly, if we look through it, the red colour is seen by transmission.

On the other hand, blue butterflies apparently never owe their colour to a pigment. If we take one of the brilliant blue butterflies from Brazil, known to zoologists as *Morpho Rhetenor*, we find that the blue colour seen so brilliantly by reflexion disappears entirely by transmission, a nondescript brownish colour being alone perceptible under these conditions. Another experiment which may be shown with this colour is its disappearance when the specimen is wetted with benzole. As the benzole dries off the specimen recovers its blue reflexion. The function of the benzole is to annul the reflexion at the front surface of the specimen, which it does by virtue of equality of refractive index.

These facts are all in accordance with the view that the blue butterfly owes its colour to interference of light; the reflexion at the front and back surfaces combining to give this interference for the less refrangible parts of the spectrum, and leaving the blue as a residuum. According to this view the spectrum of the reflexion in the ultra-violet region should show a minimum, and further on a second maximum. We find in fact that this is the case. One species (*Morpho achilles*) shows a second minimum and a third maximum further on in the ultra-violet. The original blue reflexion appears to be of the second order.

The colours of metallic beetles are of special interest and have excited considerable controversy. Some authorities attribute them to the surface reflexion of intensely absorbing matter assumed to be

present in the wing case, and in fact to be analogous to the surface reflexion of aniline colour. This view is held by the lecturer to present insuperable difficulties. In the first place the colour by absorption is not saturated, as it always is in the case of substances known to give surface reflexion. In the second place the colour of the reflexion changes greatly (from yellow to blue in the instance shown) with the angle of incidence, which surface reflexion colours do not. Lastly, when the spectrum is examined by absorption it is found that bands are present which can be identified as essentially the same over different parts of the specimen, but which *vary slightly in position*. The view taken by the lecturer is that the colour is due to interference in this case also, the peculiarities of the reflexion and also of the absorption being due to the presence of a large number of reflecting layers suitably spaced.

[R.]

Friday, March 28, 1930.

SIR ARTHUR KEITH, M.D. LL.D. D.Sc. F.R.S.,  
Manager and Vice-President, in the Chair.

SIR ERNEST RUTHERFORD, O.M. LL.D. Pres.R.S. M.R.I.,  
Professor of Natural Philosophy.

### The Transmutation of Matter.

[ABSTRACT.]

THE idea that one metal could be transmuted into another first arose among the Greeks in Alexandria in the first few centuries A.D., and spread through Europe in the Middle Ages. The search for the Philosopher's Stone, by the help of which one metal could be converted into another, was pursued with confidence and hope under the direct patronage of princes and rulers, who hoped in this way to restore their finances. Although the evidence in its support was meagre and doubtful, this idea of transmutation was very wide-spread, for it not only accorded with the desires of man, but was supported by the philosophic conceptions of Aristotle.

It does not appear to be generally known that our King Henry VI. was a convinced believer in the doctrine, and at the time of the wars with France, about 1440-50, gave patents to a number of Englishmen to convert the base metals into gold. As a result a new coinage was struck, called the "rose noble," which was distributed in France through Calais and to Scotland over the Border. The Scotch promptly retaliated by legislation to avert this danger of the introduction of a debased coinage.

With the growth of chemistry in the 18th and 19th centuries, and the proof that matter was composed of a number of distinct unchangeable elements, the idea of transmutation receded, although the idea of a primordial type of matter was never completely abandoned. The discovery of the periodic relationship in the properties of the elements revived the belief in transmutation, and Faraday remarked, "To decompose the metals, to re-form them, and to realize the once absurd notion of transmutation—these are the problems given to the chemist for solution."

The proof, in 1903, that the heavy radioactive elements were undergoing spontaneous transformation with the emission of new

radiations of a powerful type was an event of great importance, but it was soon shown that this radioactive property was confined to a few elements only, and that the great majority of the ordinary elements appeared to be permanently stable. In the meantime there was a rapid increase in our knowledge of the structure of atoms, and it became clear that in order to produce a permanent change in an atom it was necessary to remove or add a charged particle to the minute charged nucleus which governed the properties of the atom. In 1919 Rutherford showed that some of the nuclei of the atoms of nitrogen could be transformed by bombardment with the swift  $\alpha$  particles emitted by radium. Subsequently Rutherford and Chadwick found that a number of the lighter elements showed a similar effect, and in all cases a swift proton was found to be emitted in consequence of a violent collision between an  $\alpha$  particle and the atomic nucleus. Our evidence indicates that in the case of nitrogen the  $\alpha$  particle is captured during this process, and the mass of the resulting atom is greater than before. These effects manifest themselves on a very small scale, and in general only about one  $\alpha$  particle in 100,000 comes close enough to a nucleus to effect its disruption.

Transformation of an atom would occur also if an electron could be forced into a nucleus. In recent years numerous experiments have been made to change mercury into gold and lead into mercury by means of intense electrical discharges, but there is no certain evidence that any transmutation occurs by this method.

There appears to be little doubt that, if sufficiently energetic atomic projectiles were available, many of the elements could be transmuted, but only on a small scale.

Apart from the radioactive bodies, it now seems clear that a large amount of energy must be applied to produce a disruption of the nuclei of the ordinary elements. The old idea that a new source of energy could be tapped by transformation of the ordinary elements now seems untenable. There remains, however, one interesting possibility. If hydrogen nuclei—protons—could be made to combine to form a nucleus of helium, an enormous amount of energy should be emitted during the process. Unfortunately there is as yet no evidence that such a combination could be produced under conditions available in our laboratories. There seems to be clear evidence that the processes of disintegration and reformation of the atoms of the elements must be occurring in hot stars, but as yet we have no idea of the conditions requisite for such changes.

[E. R.]



Friday, January 23, 1931

THE RT. HON. LORD EUSTACE PERCY, M.A., M.P.  
*President, in the Chair*

SIR WILLIAM BRAGG, K.B.E., M.A., D.Sc.,  
F.R.S., M.R.I.  
*Fullerian Professor of Chemistry*

## THE SCATTERING OF LIGHT

MAY I preface my discourse this evening by an expression of the pleasure with which the Officers and Managers welcome the members back to the reconstructed theatre? It is eighteen months since our last meeting under traditional and familiar conditions. In the interval the theatre has been completely renewed; at one time only the four walls of the old building were left standing. Even these were found to require large repairs and reinforcements. The old interior, which was a mass of highly inflammable material, has been replaced by a construction of steel and concrete. There are now four separate means of exit to the open air, instead of the one which alone existed before. The whole building now satisfies the stringent conditions which the authorities enforce in the case of any public theatre or place of assembly.

The compulsory reconstruction of the theatre

and its exits suggested the opportunity for a remodelling of the old laboratories, and for fresh construction which should make as much use as possible of the vacant space behind the Institution. The new laboratories are a considerable enlargement and an immense improvement on the old: and great additions have been made to the means of carrying on the Institution traditions. The libraries have been extended by the construction of the large corridor which now runs from the theatre anteroom to the far library in the Davy-Faraday building, and provides ideal accommodation for our very fine collection of scientific journals. The corridor also completes the means of circulation through our reception rooms. The gallery which runs behind and under the seats of the theatre is now a place of exhibition of our large collection of historical apparatus: the construction of the theatre being such that we can thus display our treasures to advantage and be happy as to their safety.

A journey round the building can alone show the amount of work that has been done. Those of us, including our very excellent architect, Mr. Guthrie, who have been responsible for new designs and all their details have been greatly concerned, not only that nothing should be forgotten which might add to the efficiency and dignity of our Institution, but also that the traditional ideals and feelings should be maintained. In particular, we have been anxious that this theatre should, in spite of its renewal, remind us of its old self: and we believe we have so far succeeded that members as they sit here will quickly lose any impressions of change.

The cost of the reconstruction has been very

heavy. We have not been building with free hands. We had, in a strictly limited space, to fit new works on to older constructions whose imperfections added considerably to the task. We had to satisfy the very stringent regulations of the London County Council. We desired, of course, to fit the Institution for its work in every manner that experience and consideration could suggest. And at the same time we wished to preserve the old appearances and styles which give a certain character to this place and enter largely into our affections.

In all we have spent about £90,000. It is wonderful to be able to say that the whole of this great sum has been raised by various means, without public appeal, without even a general call upon our members. Part of the money has been provided by Mr. Harkness's Pilgrim Trust ; another part by various generous donors. Some of our helpers have accepted our invitation to be present here this evening. We hope that they will feel to some extent repaid for their generosity in the realisation of the help they have given to the furtherance of the Institution's aims, and the pleasure they have given to our members.

It only remains for me to express the hope of the Officers and Managers that the Members will approve of what has been done. I will now proceed with my discourse on the Scattering of Light.

## THE SCATTERING OF LIGHT.

I have thought that this subject would be of interest to you because many of the pioneering endeavours to explain its mysteries were founded on work done in our Institution and explained by our lecturers in this theatre, especially by Professor Tyndall and the late Lord Rayleigh. Of recent years the general interest in the subject has grown in a remarkable manner, because fresh experimental and theoretical developments have shown its wide importance, while at the same time the solution of some of its mysteries have opened out to us others still more fascinating. A large number of workers, in all parts of the world, are pouring out results at a bewildering rate. In the Institution we are not at the moment taking part in this particular inquiry, but the work on X-rays, which lies more within our province, is closely connected with it.

As the title of the discourse stands, it covers a very wide field indeed. If it were not that objects scattered the light that fell upon them and so sent to our eyes evidence of their presence, our eyes would be useless. Vision in the practical sense would cease. But the title has come to be understood as referring to the scattering of light by clouds of small particles as distinct from the wholesale reflection of light at the surfaces of solid bodies and liquids. In particular the problem first roused general attention in connection with the light from the sky. What is it that sends us this light, and why is its colour blue? From the attempt to answer these questions has grown an

extraordinarily interesting chapter in physical science which has far outgrown its original purpose. It tells us of the forms and characteristics of atoms and molecules, of details of solid structures, of curious properties possessed by radiation, and having given us a great fund of information leaves us at this moment full of perplexity as to some of its implications. In some ways the relations between matter and radiation are made clearer to us. In other directions we are led to see a still deeper mystery in the strange connection between the undulatory and the corpuscular theories of light.

Tyndall worked on the subject about sixty years ago. He used to send a converging beam of light into gases or vapours contained within a long tube, and he studied the appearance of the bright cone thus produced. His employment of this method was so well known and so useful that the effect was and is still known as that of the "Tyndall cone." He saw, of course, the connection between his experiment and the phenomena of sky and sea: he acknowledges his debt to Brucke, who had pointed out the connection some ten years before. One of Tyndall's tubes is still preserved here and stands on the table before you.

Tyndall rightly ascribed the effect to the presence of small particles floating within the beam of light. He recognised also that the shorter waves of light would be more readily turned aside than the longer waves, just as ripples on the surface of the sea are more easily deflected by some outcropping object, such as a rock, than longer waves or ocean swells. He thought that the light from the sky was due to scattering by

small particles floating in the air, and suggested the general diffusion of water particles. Rayleigh at that time worked out the theory of this selective scattering, showing that the intensity of the scattering of light in a medium varied inversely as the fourth power of the wave length. Later (1899) he showed that Tyndall was mistaken in requiring the presence of water vapour: the molecules themselves which composed the air might be sufficient for the purpose. About ten years later a series of observations made by Fowle at Mount Wilson showed that the light from the sky could be accounted for completely in this way. Indeed, the experiment succeeded so well that its purpose might be reversed, and the results of Fowle's measurements could be used, with the help of Rayleigh's theory, to determine the number of molecules present in a given volume of air.

The present Lord Rayleigh made further important advances in 1918. Tyndall's failure to see the possibility that the very molecules of a gas were sufficient to cause perceptible scattering was no doubt due to his imperfect removal of all extraneous light which might hinder the observation. He purified his gases of all floating matter, and was then unable to detect any trace of his "cone"; whence he concluded that no light would be scattered by a pure gas. At the top of a mountain, if no earth dust could rise so high, and there was no water vapour in the air, the sky would be black. Lord Rayleigh now doubted the accuracy of Tyndall's observations. Two facts suggested to him that it should be possible to see the scattering of light by pure air in the laboratory. The one of these was the obvious luminosity of

the sky when lit by the moon alone. Sunlight is some half-million times as strong as moonlight. If we can see the scattering of moonlight by the atmosphere, which is equivalent roughly to a five-mile layer of air at ordinary pressures and temperatures, we should be able to detect the scattering of sunlight or a strong electric light by a layer of air some half-million times less, that is to say a layer less than an inch in depth. The other fact was that the track of the searchlights so often used in the war to sweep the sky could be clearly seen when their rays had reached to a great height above the earth and must be very weak. Basing his reasoning on these observations, he made the laboratory experiment and succeeded. The scattered light was of course blue.

The light from the sky is partially polarised, a fact which was at once explained by Lord Rayleigh's theoretical treatment. In the language of the undulatory hypothesis which Rayleigh employed, the ether vibrations are perpendicular to the direction of the original ray and should remain so after scattering. If, for example, we look at a particular point of the sky, or more correctly look in a certain direction, there will be a preponderance, in what we receive, of vibrations that are perpendicular to the line joining that point to the sun. It is worth while to repeat an old experiment in illustration. A vertical beam of polarised light is shot downwards into a jar full of water containing a very finely divided suspension of mastic. The fine particles of the gum scatter the light, and the jar shows a blue column passing down its centre. If the vibrations in the incident ray are perpendicular to the line from the jar to the observer's eye, the scattering is

relatively strong. If they are parallel to that line the scattered light is weak. Observers placed at different points round the jar see different intensities. If a quartz plate, cut perpendicular to its axis, is placed on the top of the jar the planes of vibration of the various colours in the incident ray are screwed round to various amounts, the blue far more than the red. Thus one observer sees the shaft of light as of a red colour, another as of a blue : the gradually changing colours as the original plane of polarisation is made to revolve make a fine spectacle. The experiment becomes still more gorgeous if the quartz is taken away and a quantity of sugar dissolved in the jar. The rotations now take place in the jar itself and the colours vary with the depth in the water.

The undulatory theory is successful therefore in explaining the blue colour of the sky and its polarisation ; and with this go a great variety of similar effects in which scattering by an irregular distribution of fine particles is the cause. It can do more. It can explain the more complex effects where light is simply scattered by liquids and solids. Just as the purest gases can scatter through the agency of their molecules so also can liquids and solids. But there are very interesting differences. In a gas the various molecules are only occasionally under each other's influence : Boyle's law is nearly fulfilled. In that case the scatterings by the different molecules do not interfere with each other. But when the collisions are so frequent that the position of each molecule is governed partly by its neighbours, the scattered waves from one molecule interfere with those from its neighbours and the separate wave trains tend to annul each other. Thus the scattering,



mass for mass, diminishes as the substance passes from the gaseous to the liquid state, though volume for volume it increases because of the greater number of molecules in a given space. The mathematical treatment of scattering by liquids is not so simple as in the case of the gases, but it has been successfully treated by Einstein and Smoluchowski.

Their method of attack upon the problem is more general than that of Lord Rayleigh. They assume merely that the medium through which light is passing is capable of fluctuations in density, or, more strictly, in its dielectric constant. Undoubtedly such fluctuations occur in liquids and gases, and indeed in solid bodies. The atoms and molecules are never still and their relative movements are not regular. At any instant, therefore, a survey of the density would show variations from point to point, and it is this irregularity in distribution of density which causes the scattering. The survey at any one instant is peculiar to that instant: it changes continuously with time, but this additional kind of fluctuation is of secondary importance. The formula which is derived from these premises contains the compressibility of the medium as a factor. It is easy to see why the compressibility is so important. If it were zero, if the medium were one uniform mass which could not be compressed anywhere, the survey would show no fluctuations of density and there would be no scattering. On the other hand, great compressibility would lead to much scattering. In the case of a perfect gas the compressibility is merely the reciprocal of the pressure, and the formula simplifies to that of Rayleigh. But in general the compressibility is a more complicated

function. When the formula is applied to the liquid case it shows that weight for weight the liquid scatters less than the gas, while volume for volume it scatters more. The comprehensive formula shows that, as in the simpler case, the intensity of the scattering varies as the inverse fourth power of the wave length and that the scattered rays are polarised.

Experiment justifies these arguments, at least in the case when the survey of the medium, gas or liquid, has nothing to show except fluctuation of density from point to point. But now we come to the need for an interesting extension. The molecules of a gas or liquid sometimes show an orientation in respect to those of their properties which have to do with scattering. They cannot always be considered as spherical in their properties: they may be anisotropic. When the electromagnetic wave passes over such a non-spherical molecule, the oscillation set up in it may not be parallel to the vibration to the wave. The scattered light is not in such cases polarised according to the simple laws that apply when there is no anisotropy. The present Lord Rayleigh was the first to make laboratory measurements of this effect. When a ray of polarised light is sent along a tube containing the gas or liquid under investigation, the light that is scattered in a direction at right angles to the tube is almost completely polarised in the case of the inert gases, neon, argon, etc.; which gases must be very nearly isotropic.

Molecules such as  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  composed of ions which are structurally similar to argon and neon coupled to hydrogen nuclei show a feeble depolarisation. The depolarisation of the

diatomic gases hydrogen, nitrogen, oxygen, chlorine is more distinct, while in the case of  $\text{N}_2\text{O}$  and  $\text{Cl}_2$  the depolarisation is about 12 per cent. The depolarisation factor is defined as the ratio of the intensity of the scattered light which is polarised in the plane perpendicular to the incident ray to the intensity of the light which is polarised in the plane containing the ray. In the case of the inert gases this former intensity very nearly vanishes.

A simple model may make the point clearer. A few balls are mounted on flexible circular wires inserted in a wooden base so that they can wave to and fro. If the base is shaken in any direction the bells wave to and fro in the same direction. But if the wires are made so that they are bent more easily in some directions than in others, and if there is no regular arrangement of the wires in respect to these directions, the bells will vibrate in various ways when the base is shaken.

In this way the anisotropy of molecules can be studied, and all is found to go well on the assumption of the validity of the calculations based on the undulatory theory.

The theory can be carried still further with success. There is a phenomenon called opalescence which is displayed when there is an intimate mixture of two liquids or of the two states of one liquid. For instance, isobutyric acid will dissolve in water at ordinary temperatures in the proportion of about one to three. A vessel may be made to contain a layer of water containing the acid in solution, superimposed on which is a layer of the acid containing water in solution. When the temperature is raised to  $24^\circ \text{C.}$ , the acid and the water become completely intermiscible

and the boundary between the two layers disappears. At this stage the mixture becomes opalescent : a ray of light passing through it is vividly scattered. To such a case the conclusions of Einstein and Smoluchovski apply at once. The instantaneous survey must show great fluctuations in quality on account of the minute subdivision and mutual interpenetration of the two liquids. Hence arises the considerable scattering. At the same time the polarisation effect is correctly displayed.

Or again, when a liquid is brought to its critical point it becomes opalescent because the fluctuations in density caused by the intermingling of the liquid and gaseous phases give rise to strong scattering. This is readily shown in the little glass containers of liquid  $\text{CO}_2$  which are made to show the critical point. In this case it may be said that the scattering is large because the compressibility is very great. The scattering due to these fluctuations in density is so large that the polarisation of the scattered light is very complete : it is to be remembered that fluctuations in density alone, unaccompanied by fluctuations in orientations, give the simple polarisation result. When, however, the scattering of  $\text{CO}_2$  is observed under conditions away from those of the critical point there is considerable depolarisation, as already mentioned, because the orientation effect is no longer drowned by the other.

So far we have been considering cases where the light that is scattered undergoes no change of wave length. If the light from the sky is passed into a spectrometer, it shows exactly the same system of Fraunhofer lines as the light that comes directly from the sun. It is, of course, stronger

in the blue end of the spectrum. But there are also cases in which scattering is accompanied by a change of wave length ; and at this point the undulatory theory begins to be less effective in its explanations, and even to fail altogether. That it should do so after such a series of successes in the same field is most interesting. We have become accustomed to such breaks in recent years, and have realised that the orthodox theory is not the whole truth. We have taken to the quantum or corpuscular theory of light as a means of helping us to codify the cases where the other fails, and we find in the relations between the two theories a subject of never-failing interest.

Let us consider some of these cases where the scattered light differs from the original in wave length. Fluorescence is a well-known phenomenon in which the difference is obvious. A very simple way of showing the effect is to focus the spectrum upon the surface of a solution of eosin (or similar material) in a large bowl. Most of the spectrum lies like a coloured ribbon on the surface ; only the red rays penetrate the liquid without hindrance and light up the base of the vessel. The remaining rays are absorbed very soon after they have entered the solution. But the scattered rays by which we see the ribbon are a yellowish-green almost from end to end ; the energy of the original light, whatever its wave length, is converted into light of nearly the same quality. If the scattered light is examined spectroscopically it is seen to consist of a broad and diffuse band. We have the impression that light has been absorbed and remoulded through energy transformation so that its original character has been lost. The undulatory theory does

not give us any clear picture of the way in which this has been done.

Within the last two years the interest in these conversions has been immensely increased by the results of experiments made in Calcutta by Professor Raman, and extended by numerous observers in other Indian Universities and in other laboratories in the world. Raman has for some time been investigating the general problem of the scattering of light, and has made notable advances. In the course of the work, his extremely careful and ingenious technique has revealed an effect which had hitherto escaped every one's observation, though many must have guessed at its existence and looked for it.

In order to find it the source of light must give a bright line spectrum. The mercury arc has been most commonly employed. The photographic record of the scattered light then shows not only the mercury lines, but also new lines which are related to the mercury lines in a very interesting manner. They appear as satellites to the originals. If the vibration frequency of a mercury line is denoted by  $N$ , the frequencies of the new lines are of the form  $N + n$ , where  $n$  may have any one of a series of values characteristic of the scattering substance and independent of  $N$ . Thus, for example, a mercury line has, as shown in figure 1 (due to Cabannes), a set of satellites disposed symmetrically about the original intense line in the mercury spectrum. The numbers inscribed on the photographic plate express the number of waves in a millimetre. A true frequency is the number of waves in  $3 \times 10^{10}$  cm.; and is so large as to be cumbrous. It is customary to replace it, therefore, by the number in a milli-

metre or centimetre. The wave numbers of the Raman lines in the figure which show scattering by sodium chlorate are  $N + 13$ ,  $N \pm 18$ ,  $N \pm 48$ . Quartz shows a different set,  $N \pm 13$ ,  $N \pm 21$ ,  $N \pm 26$ ,  $N \pm 47$ .

Whatever sort of explanation we may try to frame, these results are at least described easily in terms of the quantum theory. From this point of view we look upon light as propagated in the

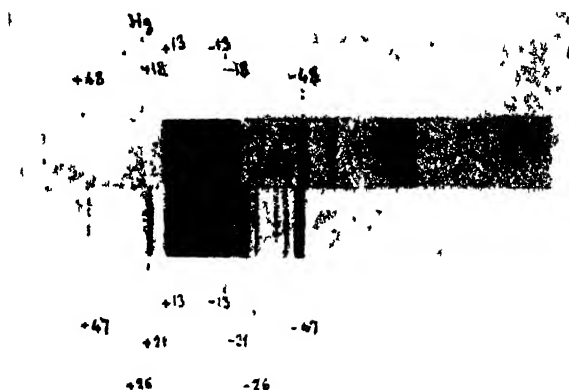


FIG 1

form of quanta or corpuscles; and the energy of a quantum is proportional to what is called the frequency in the alternative wave method of description. We say, therefore, that some of the scattered light corpuscles have gained and some lost definite quantities of energy which are characteristic of the scattering substance. These gains and losses are the same whatever the energy or frequency of the incident corpuscle.

Can these alterations of energy be connected with any feature of the substance of which they

are characteristic? There is good reason to think that they can. They should be connected with frequencies peculiar in some way to the atoms and molecules of the substance. For instance, quartz has an absorption band in the infra red at  $21\mu$  which corresponds to a wave number 47 per mm. Now it is most suggestive that the substance absorbs strongly some at least of these frequencies. They occur in the infra red, and the active prosecution of research in this region of the spectrum in recent years has provided data with which comparison may be made. When Raman's results were first published it was thought that the connection between his changes of frequency and infra red absorption was going to be very simple and direct. Further work has shown that there are complications, but still the connection appears to be real if not so obvious as it was at first believed to be. Certainly the combination of the Raman effect with infra red absorption is likely to provide a most powerful method of inquiry into molecular structure.

Thus these new studies of radiation, while adding to the interest of research, do not diminish the number of its mysteries. We are left wondering in the old way at the apparent contradictions between the most obvious ways of describing the phenomena of light. The new wave-mechanics may add to its initial successes by showing us the resolution of our difficulties. For that we must wait; for the present we can enjoy the richness and fascination of these studies which continually reward the researcher and just as often leave him free to face with new problems to be attacked.

[W. H. B.]



Friday, February 13, 1931

SIR ROBERT ROBERTSON, K.B.E., D.Sc., LL.D.,  
F.R.S.

*Treasurer and Vice-President, in the Chair*

F. LLOYD HOPWOOD, D.Sc., M.R.I.  
*Professor of Physics, St. Bartholomew's Hospital  
Medical College.*

## ULTRASONICS : SOME PROPERTIES OF INAUDIBLE SOUND

It is now common knowledge that audible sound is produced by a body vibrating in an elastic material medium, and that those parts of the medium traversed by it contract and expand rhythmically. In its transmission, sound has all the properties of a wave-motion, for it takes time to travel, has different speeds and wave lengths in different media, and exhibits the phenomena of reflection, interference, diffraction, etc., and, of course, resonance.

The intensity or loudness of a sound depends upon the extent or amplitude of the vibration set up, and its pitch upon the frequency or number of vibrations per second. Disturbances of the same type as sound waves may be inaudible either because the intensity (loudness) is insufficient or because the ear is deaf to those particular fre-

quencies : the normal range of hearing of a human being extends approximately from 20 to 20,000 vibrations per second. "Sounds" of higher frequency than 20,000 are called Super-sonic or Ultrasonic.

Many "sounds" of this nature can be generated in a variety of simple ways, as, for instance, by rubbing a resined rag along a steel wire or by tapping the end of a short rod of material with a suitable hammer. For example, a steel rod 10 centimetres long, clamped at its middle point and tapped at one end, will emit an inaudible "note" of 26,000 vibrations per second. Thus a workman who uses a small chisel or centre-punch generates ultrasonic vibrations, in addition to audible—sometimes distressingly audible—sounds ! Again, when two steel balls 1 inch in diameter collide, they vibrate after impact at the rate of over 100,000 vibrations per second.

These simple methods of producing inaudible vibrations of high frequency suffer from the serious limitations that the ultrasonic emission is discontinuous, of feeble intensity, and is accompanied by parasitic audible sounds.

Nowadays the most convenient generator of sustained vibrations is the valve-oscillator used in wireless telephony and familiar to all radio enthusiasts. By its means electrical vibrations of any desired frequency may be produced and used to excite mechanical vibrations as in a "loud speaker."

A valve-oscillator is used to excite the special form of mechanical vibrator which produces the ultrasonic vibrations with which we are now experimenting.

The vibrator itself is a disc of natural quartz crystal cut with its plane faces parallel to its optic axis and at right angles to an electric or binary axis (Fig. 1*a*).

Such a disc was shown by MM. Pierre and Jacques Curie to possess the remarkable property that when it is compressed its faces become oppositely electrified, and that its electric charges become reversed in sign if the disc is subjected to extension instead of compression. Periodic reversal of stresses is immediately followed by periodic reversal of electrification. We can

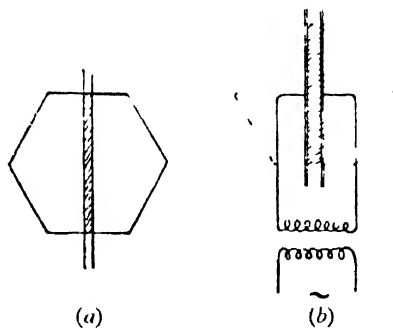


FIG. 1

illustrate this property by suspending a clock from a plate of quartz whose opposite faces are covered with tinfoil and connected through a thermionic valve-amplifier to a loud speaker. As the clock ticks it gives feeble kicks to the quartz and so causes the development of fluctuating charges of electricity, which, in turn, excite the loud speaker to broadcast the ticks to every member of the audience.

Professor Pierre Curie also showed that natural quartz, in common with certain other crystals, possessed the converse property of the one previously mentioned, namely, that if the opposite

faces of a suitably cut disc were electrified the crystal contracted in one direction and expanded in another.

This latter property was utilised by Professor Langevin of Paris to produce high-frequency sound vibrations by applying alternating electric potentials to electrodes in contact with a quartz plate (Fig. 1*b*). The plate vibrates with its

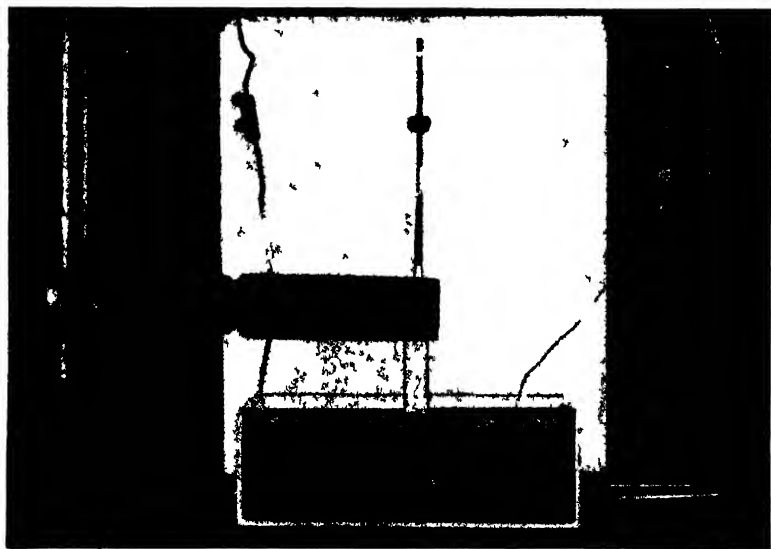


FIG. 2—Arrangement of quartz crystal and electrodes in oil bath when projecting a vertical beam of sound

maximum amplitude when the frequency of the electrical alternations coincides with a natural frequency of mechanical vibration of the quartz, in other words, when resonance is obtained.

For our experiments we use a quartz crystal cut in the form of a circular disc over 7 centimetres in diameter and nearly 5 millimetres thick. This is clamped with one face in contact

with a massive lead electrode and immersed in transformer oil contained in a small glass tank (Fig. 2). The second electrode, which is made of light copper foil, rests in contact with the other face and both electrodes are connected to a powerful (3 kilo-watt) valve-oscillator, executing half a million vibrations a second, or more.

For some purposes the disc is placed with its plane faces vertical and projects a horizontal beam of sound ; for others, the plane faces are horizontal and the sound beam is projected upwards (see Fig. 2).

The use of the oil permits the application of very high voltages to the crystal, and also makes it easy to subject small objects to the influence of the very intense vibrations which are necessary to produce some of the effects to be shown.

### *Experiments with a Horizontal Beam of Sound.*

Following Professor R. W. Boyle the production of *stationary waves* in the oil is rendered visible by the striæ formed in coke dust scattered on a horizontal opal-glass plate placed in the sound beam.

The distance between successive striæ, *i.e.* half a wave length of the sound in oil, is here between 1 and 2 millimetres. This wave length is so short in comparison with the dimensions of the crystal and other objects in the tank that these waves exhibit the directional properties ordinarily associated with light waves. Thus, by using plane and curved reflectors the well-known laws of reflection are verified. In the case of a cylindrical reflector the oncoming

and reflected waves combine to produce the pattern shown in Fig. 3.

In the same way refraction of sound waves by prisms and lenses can be demonstrated. Figs. 4A and 4B show how sound waves travelling through pentane, and falling on a parallel layer of transformer oil, will be transmitted if the angle of incidence is less than a certain value (Critical



FIG 3 —Interference pattern obtained by reflection from a concave cylindrical surface

Angle), but totally reflected if it exceeds this value (Total Internal Reflection). In fact, most objective optical phenomena, except polarisation, can also be faithfully paralleled by these means.

Such experiments as these lend support to the thesis that the best way to teach the principles of optics is to use the properties of ultrasonics to illustrate them.

Another application of the coke-dust method

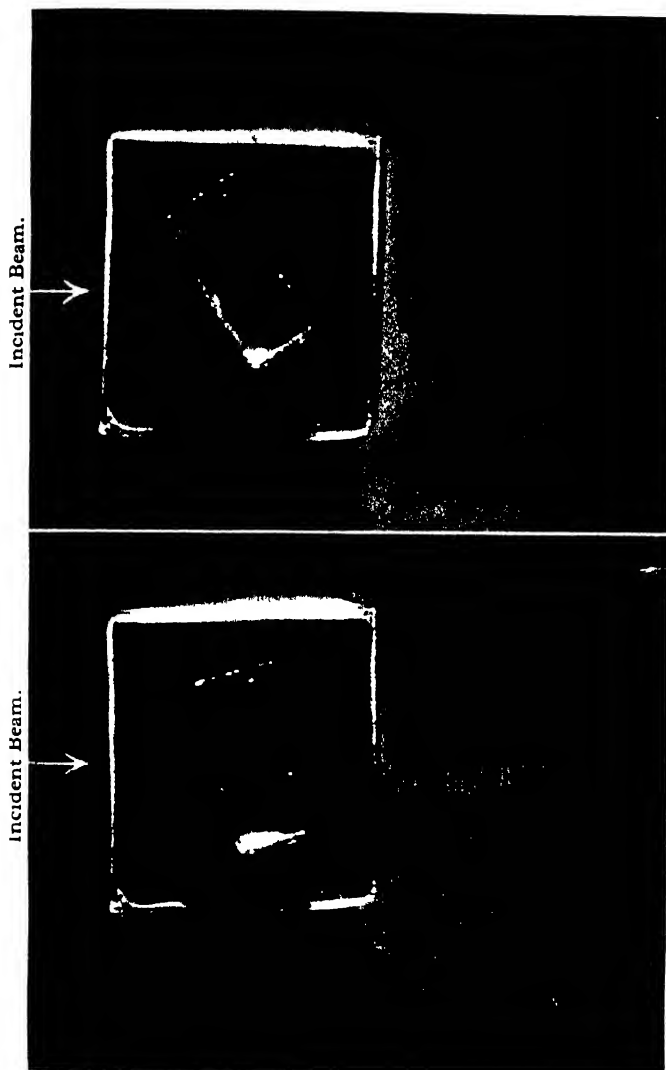


FIG. 4A.—Shows transmission of ultrasonic waves through layers of pentane and transformer oil for angle of incidence less than critical angle. The outer vessel contains pentane and the inner oil.

FIG. 4B.—Shows total internal reflection of ultrasonic waves at surface between pentane and transformer oil. Angle of incidence greater than critical angle.

of showing stationary sound waves is to the study of architectural acoustics. Members of the Royal Institution know that their lecture theatre behaves as a *whispering gallery*. Fig. 5 shows how this effect can be studied quite satisfactorily on a very small scale model by



FIG. 5 —Model of lecture theatre of Royal Institution, showing "whispering gallery" effect, illustrated by stationary waves of ultrasonic "sound" of 2 mm wave length. Notice how waves hug wall

using ultrasonic vibrations instead of audible sound. The clinging of the waves to the circular wall is very marked.

*The Pressure of Radiation* to which an obstacle is subjected when sound waves fall upon it is shown by the rotation of the vane of a torsion pendulum placed in the horizontal ultrasonic



beam. This affords a convenient method of estimating the intensity of the sound, which can be used for measuring the acoustic reflection and transmission coefficients of different materials.

*Experiments with the Ultrasonic Beam directed towards the Surface of a Liquid.*

The properties of ultrasonic waves which we have so far described were predicted from theoretical considerations before they were experimentally demonstrated by Langevin, Boyle, and others.

Remarkable and hitherto quite unforeseen effects can, however, also be produced by ultrasonic vibrations when these are of great intensity and very high frequency.

With the crystal arranged as shown in Fig. 2, the ultrasonic beam is confined mainly to the column of liquid between the upper crystal face and the surface of the oil. Professor R. W. Wood and Mr. Loomis have shown that under these circumstances the great concentration of energy causes the amplitude of vibration of the disturbed particles of liquid greatly to exceed the amplitude of vibration of the crystal itself.

At the same time the pressure of radiation produces on the surface a mound of oil, several centimetres or even inches in height, which erupts droplets like a miniature fountain. On plunging vessels of appropriate form into this mound of oil, vibrations of great intensity may be communicated to the walls of the vessels, or, through the walls to liquids contained in them. If a test-tube containing water is partially immersed in the oil, bubbles of dissolved gas are usually

liberated in it (Fig. 6). These behave in a peculiar manner. For moderate intensities of vibration the bubbles form slowly and remain practically stationary at the nodes of the waves formed in the water. As the bubbles grow in size they oscillate and tend to rise to the surface



FIG 6 — Expulsion from water of dissolved air as bubbles

in an irregular zigzag manner as if they were going up a staircase. For still greater intensities we have found that no visible gas bubbles can either exist or be formed. This is probably to be explained as follows. The density of the gas being much less than that of the liquid, the bubbles formed at low intensities must experience the

same forces and therefore have greater amplitudes of vibration than the particles of liquid they displace. The result is that at high intensities they are shattered and so dispersed through the liquid as to become and remain effectively in solution.

*Cavitation* can be produced in liquids such as pentane or benzene, by using a U-tube closed at one end, the closed limb being filled with the liquid, and placed in the mound of oil above the vibrating crystal. The bubbles of vapour formed in the interior of the liquid and collected in the closed limb can be again condensed into liquid by raising the air pressure on the open limb. Using now an inverted U-tube or  $\Omega$ -tube, which is completely sealed up and contains liquid in one limb only, we observe the rapid vaporisation of liquid in the agitated limb and its deposition as liquid in the previously empty limb. This might appropriately be called *Acoustic Distillation*.

On substituting for the inverted U-tube a similar tube which contains a little dry lycopodium powder but is otherwise highly evacuated, an astonishing result is obtained. The powder moves in this case *towards* the limb which is subjected to the more intense vibration! This last effect is one of a number of phenomena due to the transverse vibrations of various types set up in the walls of the vessel itself. Another of these effects is the formation of ripples in the oil splashed on the tube and the repulsion of the oil drops away from the source of disturbance.

The most striking thing, however, about the oil drops is their behaviour at a constriction, or

at the narrower parts of a tube such as is shown in Fig. 2. High inputs of ultrasonic energy cause intense local heating at such places and the oil is thrown off as spray and jets of vapour as from diminutive geysers. If the tube is drawn off into a fine fibre and firmly grasped between the fingers a severe burn is experienced. In addition to the calorific effects produced in the walls of various containers, the absorption of sound energy which occurs in their contents causes appreciable rises of temperature in them also.

Amongst other effects which we can produce by our installation we may cite the acceleration of certain chemical reactions, the flocculation of suspended matter, and the emulsification of oil and water, etc.

Most of the effects which we have shown as obtainable with the ultrasonic beam directed towards the surface of a liquid were discovered by Wood and Loomis in America. Acoustic distillation, the anomalous movement of lycopodium powder, and the non-liberation of bubbles from water with very high intensities are, we believe, described now for the first time.

### *Biological Effects of Ultrasonics.*

Some fifteen years ago, while carrying out experiments at sea, Langevin and his co-workers observed that fish which swam into a beam of ultrasonic waves were disabled or killed. Being informed at that time of this mysterious occurrence, the lecturer determined that when circumstances permitted he would investigate the matter.

During the past few years, with the invaluable help of some of his colleagues and friends, he has been able to do this. Quite independently, Wood and Loomis covered much the same ground. Let us notice first what happens to an object whose dimensions are large compared with the wave length of the sound waves which irradiate it. One result can be seen from Figs. 7A and 7B. These are reproductions of microphotographs of a freshwater plant —*Nitella*. The irradiated specimen shows how certain regions in a cell are denuded of their chloroplasts which are then piled up in other spots. A gentler irradiation merely causes the streaming of the protoplasm to cease either temporarily or permanently according to the duration of exposure. The mechanical action which has taken place here can be understood when it is realised what occurs in the water in which the plant is immersed. Although the excursion of a disturbed particle during a single vibration is only equal to a few wave lengths of light, these vibrations, occurring at the rate of nearly a million times a second, cause the maximum velocity of the particle to be very high ; its maximum acceleration may become as great as 10 kilometres per second per second. We have, in effect, a *micro ultra-centrifuge*, which subjects specimens to very intense though highly localised forces.

This explanation accounts quite satisfactorily for certain other effects we have obtained, such as the breakdown of the red blood-corpuscle and the disruption of *Planaria* and similar small living organisms. The same explanation may possibly account for the behaviour of an irradiated muscle-nerve preparation and the arrest or retardation of

the beating of the isolated frog's heart and embryonic heart of a chick.

The muscle-nerve preparation immersed in a stream of Ringer's solution was stimulated electrically, and its contractions recorded in the usual



FIG 7B — *Nitella* after exposure to ultrasonic vibrations ( $n=750,000$ )

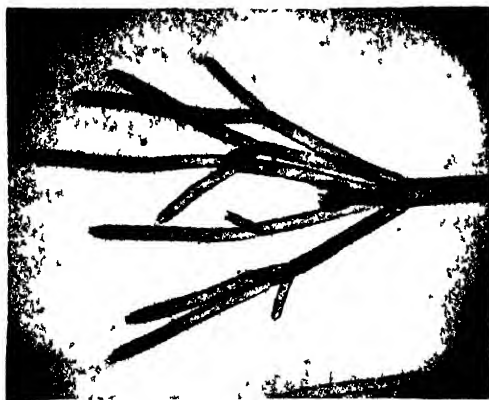


FIG. 7A — Normal *Nitella*

manner. Fig. 8 shows the decrease in its response when the sound field is "on," and also the lag in the return to normal when the field is turned "off."

Some further explanation than the one already given is required to explain the action on bacteria and viruses—bodies which are of microscopic and ultra-microscopic dimensions.

We have found that the agglutinating power of certain streptococci is increased after irradiation, but the virulence of a strain of pneumococcus was unchanged or changed in an indefinite manner. (Preliminary experiments with Bacteriophage have given a *nil* result.)

Positive effects have been obtained with one virus. Table I shows the effect of ultrasonic vibrations in increasing the potency of the virus



FIG. 8—Muscle nerve excitation as affected by ultrasonic vibrations. AB = normal excitation. BC shows response during exposure to ultrasonic beams, CD shows lag in recovery.

of Vaccinia. Through the kindness of Dr. Mervyn Gordon the irradiated and control lymphs in various dilutions were used to vaccinate the skin of a rabbit. The "takes" were recorded after the requisite period of time had elapsed for the characteristic lesions to be produced. Two series of experiments were carried out, the lymph in the first case being given only one-fifth of the exposure given in the second case.

It will be noticed that the result is the same in both cases. Presumably the effect of the exposure was merely to disengage inert foreign material from the virus so that the latter could exhibit its intrinsic potency.

TABLE I  
EFFECT OF ULTRASONIC VIBRATIONS ON VACCINIA VIRUS  
(Frequency 700,000)

<i>Dilution</i>	<i>1st Expt.</i>	<i>2nd Expt</i>	<i>Control</i>
1/1	†	†	
1 10	†	†	
1 50	†	†	
1/100	†	†	
1/500	•	•	
1 1000	†		
1 2000	—		

We have seen that fish may be killed by means of inaudible sound waves. With so many effects occurring simultaneously—the breaking up of blood corpuscles; liberation of dissolved gases; paralysis of muscle and nerve; localised mechanical action and heat production—this should no longer surprise us!

In conclusion, some anxiety may be removed from the minds of those who have followed these experiments if they are told that there is here no menace to human life. The vibrations were of necessity produced in a liquid because at these high frequencies the waves are so rapidly attenuated in air that their propagation through it is practically impossible.

[F. L. II.]

Figs 1, 2, 3, 7 and 8 are reproduced (by the courtesy of the Board of the Institute of Physics) from the *Journal of Scientific Instruments*, Vol VI, No. 2.



Friday, March 20, 1931

SIR ROBERT ROBERTSON, K.B.E., D.Sc.,  
LL.D., F.R.S.,  
*Treasurer and Vice-President, in the Chair*

E. N. DA C. ANDRADE, D.Sc., Ph.D., M.R.I.,  
*Quain Professor of Physics in the University  
of London*

## SOUND, SAND, AND SMOKE : NEW LIGHT ON OLD PROBLEMS

MODERN physics may with some justification be said to consist in the study of vibrations. The vibrations are often of a very mysterious character, about which it is considered indelicate to ask too closely. The study of such vibrations, under the term of "wave mechanics," has often received attention in discourses in this our Institution, and the only help towards picturing the processes involved which the experts of these advances offer is a certain analogy with sound vibrations. You are told that vibrating plates have certain definite modes of vibrating in segments, each mode corresponding to a definite note or frequency, and from this you are invited to consider the discrete solutions so fundamental for wave mechanics. Sound vibrations are, luckily, very easy to demonstrate and understand, since they deal with material media ; the

frequency of the vibrations is evident to our ears as a definite note, and the mode in which the source of sound is vibrating can be made evident to our eyes in certain very simple ways. A common way is to use a powder of some kind—sand, powdered cork, the light seeds of lycopodium—and observe how the sound vibrations distribute it. To-night I am going to discuss the use of particles of various kinds in elucidating sound problems, and I hope to show you that, according to the nature of the particles, very different effects are produced and very different kinds of information may be won. Incidentally I shall show on the screen, so that all can see them, the different modes of vibration of plates which are so often used as illustrations by the disciples of  $\psi$  and  $\bar{\psi}$ .

The first to use powders in sound problems was Chladni (Fig. 1), who used sand to indicate the method in which a rod vibrating transversely divides itself up into segments. His first experiments were published at Leipzig in 1787, while the first edition of his important book, *Die Akustik*, was published in German in 1802, and the French edition, dedicated to Napoleon, in 1808. He had noticed that a plate of glass or metal gave a different sound according to the place where it was struck, and he had also read of Lichtenberg's electrical dust figures. This, in his words, "made me presume that the different vibrating motions of a sonorous plate might also present different appearances if a little sand or some other similar substance were spread on the surface." By clamping the plate between points, and bowing at an edge, Chladni found that he could produce a variety of figures,

the exact figure produced being determined by touching the plate and by bowing at suitable places. The sand forms in a pattern of lines, and, as Chladni realised, indicates regions where the plate is at rest, or nodal lines, as they are called. This method of exciting the plate by bowing is that, as far as I am aware, always adopted hitherto to exhibit the figures.

To show you the figures to-night I have, however, adopted a new method, which enables us to project the figures on a screen. The plate used is made of steel, and beneath it is a small magnet, through which the rapidly alternating current from a valve oscillator is sent. The frequency of the current is controlled by a condenser in the usual way. If I now vary it continuously, every time that I hit upon a frequency proper to the plate there is a vigorous vibration, and you see on the screen a sand figure which is immediately formed, and hear at the same time a note that corresponds to the particular method of vibration so indicated. This method enables the vibrations of the plate to be studied with great ease, and seems adapted to decide difficult points, since, as the late Lord Rayleigh has pointed out, vibrations excited by a bow are not, strictly speaking, free.

Speaking generally, the more complicated the figure, the higher the note; that is, the smaller the regions enclosed by the lines of no motion the more rapid is the vibration of the plate. A precise example of this is furnished by a bar. If a long slab of steel be supported on knife edges placed at calculated spots it can be thrown into vibration by a magnet in the same way as the plate, and the sand will indicate nodal lines



*Dr. E. F. F. Chladni.*

FIG. 1.—Portrait of Chladni, from the first edition of *Die Akustik*.

transverse to the length of the bar. In this way we can see a bar vibrating in three, four, five, six or more segments, and hear that the note becomes higher as the number of segments increases. The supporting edges must be arranged under points which are natural nodes of the bar. Bars supported in this way make up the unpleasant instrument known as the xylophone.

The question as to why the sand particles go to the nodal lines has never been properly discussed, but it is an interesting one. A particle can only move on a plate if the vibration is so rapid that there is actually no contact between plate and particle at one stage of the motion. When the plate is travelling downwards from its equilibrium position to the lowest position it is slowing up, and the pressure of the particle upon it will be increased, as it will likewise as the plate subsequently travels up to its equilibrium position, but as it moves from its equilibrium position to the highest position it is travelling more and more slowly, and is, so to speak, falling away from under the particle. More precisely expressed, if the downward acceleration is greater than  $g$  as it travels up, then the particle will leave the plate with the (upward) velocity which the plate has when the particle is last in contact with it. It will be thrown outwards to a node.\*

With Mr. D. H. Smith I carried out a few experiments to check this point. Firstly, using a square plate, we found that if the vibrations have less than a certain amplitude, controlled by

\* Under certain conditions the particle may, on its descent, strike the plate when it is in such a position that the particle is thrown toward the antinode. This point is discussed in *Proceedings Physical Society*, 43, 405, 1931.

a variable resistance in the magnet circuit, there is no motion of the sand, no matter how long the plate is left in vibration. Secondly, if the vibrations are made a little more vigorous the sand does indeed move, but not to the nodes ; it only clears a space in the neighbourhood of the point of greatest motion, the sand grains moving to a perfectly defined boundary line, as shown in Fig. 2. If the intensity is still further increased the clear area increases in size, until finally the whole plate is free of sand except for narrow regions in the neighbourhood of the nodal lines. Figs 3, 4, and 5 show successive stages reached with increasing intensity.

Now if we know the frequency of the vibration and the amplitude at a given point, we can calculate the maximum acceleration of the plate at that point. By focussing the microscope on a speck on the edge of the plate we measured the amplitude at the boundary line of the sand region in such a case as is shown in Fig. 2. The result was that the point where the sand stopped was a point where the greatest acceleration of the plate was a little greater than  $g$ . More accurate experiments were carried out with a vibrating bar and particles of broken glass. With this arrangement the acceleration at the point where the particles just did not move was found to be, as an average of four independent measurements, 978 cms./sec.<sup>2</sup>, which is, within experimental error, the value of  $g$ .

I can show you the case of the bar on a large scale by means of a plank about ten feet long thrown into vibration by an arrangement similar to that used for ringing an electric bell, a steel stud fastened to the plate being attracted by a



FIG 2



FIG 3



FIG 4

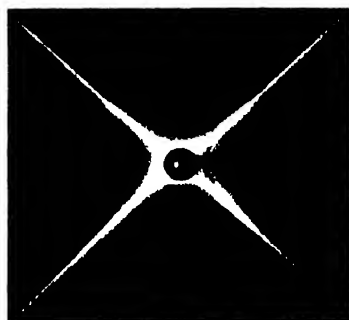


FIG 5

Sand figure formed at a given frequency with four different intensities,  
increasing from Fig 2 to Fig 5

*(Reproduced by the courtesy of the Physical Society)*

magnet. Small blocks of blackened wood placed on the plank then move towards the nodes, stopping short of them just as does the sand on the steel bar.

We now come to another interesting point concerning the use of fine particles to indicate the vibration of plates. Savart found that a fine light powder, such as lycopodium, behaved quite differently from sand ; instead of going to the nodes it heaps itself up at the places of greatest motion. I can show this with the square plate which you have already seen. We strew a mixture of black emery powder and pale yellow locopodium powder on the plate, and then throw it into vibration. The heavy black powder goes to the nodes ; the light pale powder separates out to the antinodes. Just a hundred years ago Faraday showed that the movement of the light powder was due to currents of air set up by the vibration of the plate, which carried the powder along. By placing the plate in a vessel with a plate-glass top, and exhausting the air, I have proved that, in the absence of air, lycopodium powder on the plate goes to the nodes, and not to the antinodes. The behaviour of sand and lycopodium in air affords an excellent example of a general point which I wish to make, namely that before we can decide what the movement of a particle in air tells us we must carefully consider the nature of the particle, and in particular its inertia in relation to its size.

I now want to pass on to another case where particles have been used to reveal sound vibrations, namely the familiar experiments of Kundt. The original experiment was carried out in the following way : a long glass tube is closed at one



end by a close-fitting cork, which can be moved so as to vary the length of the enclosed air column, and at the other by a loosely-fitting cork at the end of a rod clamped at its middle. The rod can be brought into vibration by stroking, and communicates its vibrations to the column of air enclosed in the tube. Now if light powder, cork dust, or lycopodium seed is put into the tube, and the air is thrown into vibration, it takes up a remarkable appearance. A series of rings, or, as I call them, eyes (see Fig. 6), is formed at equal intervals, marking out the nodes. If the tube is set to resonance, that is, if the vibration is intense, instead of eyes we have little heaps of dust formed at the nodes. If a heavy powder, such as sand or iron filings, is used a series of sharp ridges can be formed, separated by patches of undisturbed dust at the nodes, as is shown in Fig. 7.\* With any of the patterns obtained nodes are clearly marked out by the dust which permits of measurement of the velocity of sound, so long as the frequency of the vibration is known, this frequency being calculated in the familiar way from the length of the exciting rod.

The disadvantages of Kundt's method are many: to obtain absolute velocities it is necessary to know the absolute velocity of the sound in the material of the rod, or in a standard gas, which practically reduces the method to one of comparison; high frequencies only can be obtained with rods of practicable length; the intensity of the vibration varies throughout the sounding of the note; the dust figures can only

\* This figure was obtained with cork dust, the differences of pattern having been traced to differences of intensity, so that any of the figures obtained by earlier workers with different powders can be obtained with one kind of powder.



FIG. 6 A nodal ring, or  
"eye"



FIG. 7 Two ridge groups  
separated by a node

be considered in detail after the sound has ceased. The new technique of the valve oscillator enables us to secure conditions which permit accurate absolute measurements of frequency ; a wide range of frequency ; and a state of steady intensity which enables the figures to be studied under perfectly definite conditions. To excite the vibrations a loud speaker sounding unit is fastened to the end of a tube, and the current from a valve oscillator passed through it. The frequency can be measured by passing the current through a string galvanometer and taking a photographic record of the vibration, while the wave form can be examined by the aid of a cathode ray oscillograph. The intensity and frequency can be varied at will.

When cork dust is introduced into the tube there are always, mixed with the coarser particles, some very fine particles indeed. These float in the air, and are so light that they are carried rapidly to and fro by the air vibrations, presenting the appearance of little lines with a bright spot at either end, as shown in Fig. 8. The length of these lines might be supposed at first to give the amplitude of the vibration. However, whether a particle indicates the full extent of a vibratory motion of a fluid in which it is floating depends upon its size, upon its mass, and upon the frequency of the vibration. Calculation shows that while even the finest cork particles ordinarily found will not follow to the full extent the motion of air vibrating a few hundred times a second, smoke particles are small and light enough to do so. Luckily, the individual smoke particles can be quite easily seen through the microscope, and they are drawn

out into bright lines when the air is thrown into vibration ; the length of these lines can, with care and experience, be measured accurately with a microscope, and so we have at our disposal a method of measuring the amplitude of the air vibrations.

If you observe, then, a smoke particle or a drift of smoke particles, you can be confident



FIG. 8.—Small cork particles presenting the appearance of lines owing to rapid vibration

that the smoke particles are following in all respects the motion of the air. They act as tracing points. Heavier particles do not act as tracing points : the air washes to and fro over them, to some extent. You cannot gather from the movement of a cork particle how the air may be moving in the absence of that particle. Neglect of

the essential fact that cork particles cannot act as tracing points has caused much confusion.

(The movement of dust particles in a sounding tube, and in particular the formation of sharp ridges, the formation of eyes at the nodes, and of a sharp disc at the antinodes (Fig. 9) were here demonstrated by means of cinematograph films taken by the lecturer.)

To explain the various phenomena that occur in the tube, namely the ridges, the eyes, and the antinodal disc, it is necessary in the first place to

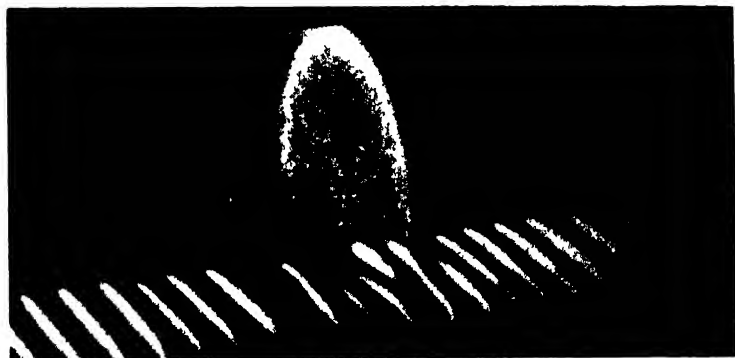


FIG. 9.—The new phenomenon of a sharp antinodal disc.

study the motion of the air in the tube in the absence of all dust particles. This can be done by the introduction of smoke. When the air is set into vibration the tube appears divided up into sections, with boundaries at the nodes and at the antinodes. On close examination the cause of this division is found to be a general circulation of the air, from antinode to node along the walls of the tube, and from node to antinode up the centre, a photograph of a longitudinal section of such a circulation being shown



FIG 10.—Node to antinode circulation in a dust-free tube.

in Fig. 10. This circulation is disturbed if precautions are not taken to avoid convection currents, but still exists in a distorted form.

This, then, is one phenomenon with which we have to reckon. If we now turn to the ridges of dust, one feature which I observed is that they do not form unless the intensity of the sound is greater than a certain value. This suggested that the formation might be due to a change from vortex-free to vortex-motion of the air, for it is characteristic of such a change that it always occurs when the velocities of motion exceed a certain value. Accordingly an attempt was made to observe a vortex motion round an obstacle in the sounding tube. A cylinder was used in the first instance, and smoke introduced to trace the motion of the air. Suitable illumination enabled a cross-section to be isolated for observation. When the air was set into vigorous vibration a beautiful vortex system, as shown in Fig. 11, formed round the cylinder. If the intensity of the vibration is reduced the vortex shrinks; below a certain

intensity no vortex at all is formed. A vortex system similar in many respects is formed round a spherical obstacle.

On the basis of these two observations the dust phenomena in a sounding tube can be explained. The ridges are due to vortex systems formed round the dust obstacles: the eyes and the antinodal disc to these vortices in combination with the general circulation, in a way that

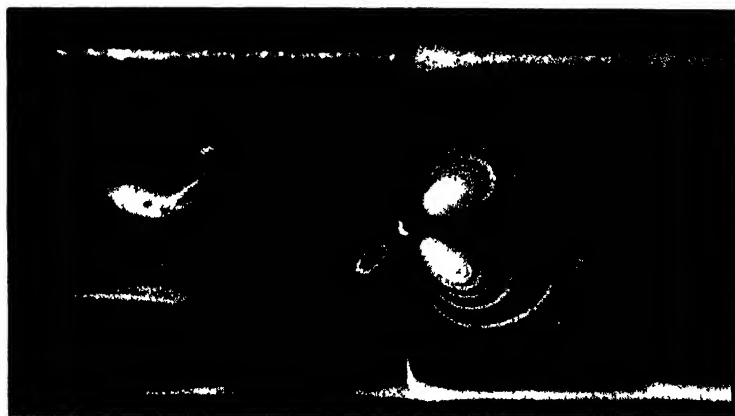


FIG 11 Vortex system formed round a cylinder in vibrating air

will be explained in detail in a forthcoming publication.

I am afraid that the experiments described this evening deal with problems that are now considered old-fashioned. I can only justify them by pointing out that the processes which go on in a sounding tube must be understood before the tube can be used to determine the velocity of sound accurately, and that the velocity of sound gives us the ratio of the specific heats, which is not without interest in certain problems connected with the quantum theory. [E. N DA C. A.]

Friday, March 27, 1931

WILLIAM HENRY ECCLES, D.Sc., F.R.S.  
*Manager, in the Chair*

LORD RUTHERFORD OF NELSON, O.M., M.A.,  
D.Sc., F.R.S., M.R.I.  
*Professor of Natural Philosophy ; Cavendish  
Professor of Physics, University of Cambridge*

## HELIUM AND ITS PROPERTIES

[ABSTRACT]

THE history of the discovery of helium presents some features of unusual dramatic interest. During an eclipse in 1868, Jansen and Lockyer noticed that the visual spectrum of the sun's chromosphere showed a bright yellow line of unknown origin. Later it was found that this line and others that accompanied it appeared not only in the sun but also in many of the stars. Lockyer suggested that these lines were due to an undiscovered element to which he gave the name helium. Shortly after the discovery of argon, Sir Henry Miers sent a letter (February 1st, 1895) to Ramsay pointing out that the American analyst Hillebrande had observed that a considerable quantity of gas, supposed to be nitrogen, was liberated by solution of certain minerals



containing uranium. Miers suggested that the gas might prove to be argon and not nitrogen. Following his suggestion, Ramsay purchased about one gramme of the mineral Cleveite from a dealer for three shillings and sixpence and proceeded to purify the gases evolved and to examine their spectra. A number of new lines were observed and a spectrum tube containing the new gas temporarily called Crypton by Ramsay was sent to Sir William Crookes for a detailed study of its spectrum. Crookes reported tersely, "Crypton is Helium; come and see it." Less than two months had elapsed from the receipt of Miers's letter to the announcement in the French Academy, on March 26th, 1895, of the discovery of helium on the earth—a discovery of profound significance to the development of Physics. It was soon shown that helium was a monatomic gas of density about twice that of hydrogen and of atomic weight 4. We now know that it is the first of that remarkable group of inert monatomic gases, viz. helium, neon, argon, krypton, xenon, and the radioactive emanations which have played such an important part in helping to fix the arrangements of the electrons in the outer atom.

In 1903 Ramsay and Soddy found that helium was produced by the transformation of radium and, as a result of a series of researches, Rutherford showed that the alpha particles which are ejected with great velocity from radioactive atoms were identical with helium nuclei. It is probable that the greater part, if not all, of the helium found in the earth and in the natural gases escaping from the earth owes its origin to the  $\alpha$ -particles expelled from the radioactive

elements during their transformation in the earth's crust.

It now seems clear that the helium nucleus of resultant charge 2 is remarkably stable and is in some way built up by the combination of four protons and two electrons. The loss of mass in this combination shows that a very large amount of energy, probably in the form of penetrating gamma rays, is emitted during the process. It can be calculated that the energy released in the formation of one pound of helium from hydrogen corresponds to the energy liberated in the complete combustion of 10,000 tons of coal. There can be no doubt that helium is formed from hydrogen under some, as yet unknown, conditions in the stellar system. However, it has not yet been found possible to produce helium from hydrogen under laboratory conditions. Millikan claims that the absorbable part of the cosmic rays must be attributed to the radiation emitted in the formation of helium in the depths of space.

The  $\alpha$ -particle or helium nucleus has proved of great importance in extending our knowledge of the structure of nuclei, and it is now believed that the nuclei of the heavier elements are composed mainly of  $\alpha$ -particles and electrons, although a few free protons may also be present. The bombardment of light elements by swift  $\alpha$ -particles has given us the first definite proof of the transformation of some of the ordinary elements by artificial methods.

Helium is the most difficult of all gases to produce in liquid form. This was first accomplished by the late Professor Kammerlingh Onnes in his laboratory at Leyden in 1908 by using

liquid hydrogen as a cooling agent. Helium liquefies at a temperature of about  $4^{\circ}$  absolute, and is a clear colourless liquid of density about 0.15. In recent years, by using helium under pressure, Professor Keesom of Leyden has succeeded in solidifying helium. By the evaporation of liquid helium at low pressure, temperatures as low as  $1^{\circ}$  absolute have been obtained. Liquid helium thus provides a suitable method for the study of the effect of low temperatures on the properties of matter. One of the most striking observations is that certain metals become superconductors at such low temperatures and show little if any resistance to the passage of an electrical current. Several cryogenic laboratories have been instituted for the study of the effects of low temperatures on matter. Apart from the well-known and well-equipped Laboratory at Leyden, Professor J. C. McLennan liquefied helium in the University of Toronto in 1923, while in 1925 a similar Department was instituted in the Reichsanstalt, Berlin. Researches in the properties of matter at the lowest possible temperatures have already added widely to our knowledge in a number of important directions.

Helium is present in our atmosphere in small quantity, about one part in 185,000 by volume. In the early days most of the helium used for experimental purposes was obtained by heating radioactive minerals and particularly the mineral thorianite from Ceylon. It was also found that helium was often present in considerable quantity in the gases escaping from hot springs and the natural gases from the earth's crust.

In 1914, Sir Richard Threlfall suggested to the Board of Inventions of the Admiralty that,

on account of its lightness and non-inflammability, helium might prove of great service for balloons and airships. Professor J. C. McLennan, of the University of Toronto, was asked to initiate experiments to see whether helium could be separated in quantity from the natural gases escaping from the earth in certain districts of Canada which were known to contain about one per cent. of helium by volume. Arrangements were made on a semi-commercial scale to purify the helium by liquefying the methane and other gases present. The impure helium was concentrated in the non-liquefying portion. In this way, many thousands of cubic feet of helium were prepared and transported in cylinders at high pressure. About the same time, the Bureau of Mines of the U.S.A. began similar experiments on a large scale, using the natural gases of Texas which were rich in helium. Large quantities of helium were separated by liquefaction methods, and the cost of the helium was found to be sufficiently low to use it in airships in the place of hydrogen. Apart from the cost of transport, the expense of separation of helium decreases with the concentration of the helium in the natural gases. The commercial prospects of the use of helium in airships and other purposes have led to a search for rich concentrations of helium.

While most natural gases contain less than 1 per cent. of helium, much richer mixtures have been recently found by boring. One source in Grand County, Utah, had a helium content of 7 per cent. Another was found in Colorado yielding as high as 8 per cent. The gas appears at a depth of about 950 feet in what is known as

the Wingate sand. The Helium Company have erected a plant at Thatcher, Colorado, for purification of the helium obtained from this source. Analysis shows that the gas contains 15 per cent. carbon dioxide, 8 per cent. helium, 1.75 per cent. methane and the rest nitrogen. The plant installed has a capacity of about 600,000 cubic feet of the gas per day, corresponding to a possible annual production of 12 million cubic feet of helium. With such a rich helium mixture, the cost of separation should be much less than in the plants treating the natural gases of much lower helium content.

It may be possible that similar rich concentrations may be found on the eastern slopes of the Rocky Mountains in Canada. A small gas field was found a few years ago not far from Toronto which had a content of 0.8 per cent. helium. The rights of those wells have been secured for the University of Toronto in order to have an ample supply of helium for cryogenic experiments in the Laboratories.

At the time of its discovery, helium was considered to be a rare gas and a litre of helium was a precious possession. The helium originally employed by Kammerlingh Onnes for the liquefaction of helium was painfully obtained by heating radioactive minerals. This is in striking contrast to the position to-day, when the annual production of helium is measured by millions of cubic feet and where sufficient quantity will be available at a comparatively low cost for filling several large airships now in course of construction.

A number of experiments were shown during the lecture in illustration of the properties and

modes of separation and purification of helium. The difference of density between hydrogen and helium was shown by filling two similar light balloons. The high heat conductivity of helium compared with air was shown by the relative heating of platinum wires immersed in the gases when the same electric current was passed. A special helium spectrum tube was constructed capable of carrying a heavy current from a generator at 2,000 volts. When filled with helium at low pressure, this gave a brilliant luminosity and the characteristic spectrum of helium was thrown upon a screen by means of a concave grating.

The rapid diffusion of helium through a porous pot was illustrated and an estimate of the molecular weight of helium was made by comparing its rate of diffusion with that of hydrogen. The new valve methods for detecting single  $\alpha$ -particles were shown and the entrance of each particle into the detecting vessel was arranged to give an easily audible click in a loud-speaker, while the entrance of  $\alpha$ -particles at the rate of about 1,000 per minute gave a continuous roar. It was pointed out that, even with such a comparatively rapid rate of counting of  $\alpha$ -particles giving such a marked effect in a loud-speaker, about  $5 \times 10^{10}$  years would be required before one cubic centimetre of helium could be obtained from the accumulated  $\alpha$ -particles.

Finally, an experiment was shown illustrating the process of separation and purification of helium from a radioactive mineral, samarskite. Some of the powdered mineral was placed in a quartz tube in series with a charcoal tube immersed in liquid air, a heated tube filled with

copper oxide, a drying tube and finally a large spectrum tube. The whole apparatus was first exhausted to a low vacuum; on heating the quartz tube with a blow-pipe, the occluded helium was liberated from the mineral and all gases but helium were removed by the charcoal and other agents. The spectrum tube, excited by a coil, in a few minutes showed the characteristic brilliant glow of pure helium.

[R. OF N.]

Friday, May 15, 1931

A. CHASTON CHAPMAN, F.R.S.  
*Manager, in the Chair*

J. C. PHILIP, O.B.E., D.Sc., F.R.S.  
*Professor of Physical Chemistry, Imperial  
College of Science and Technology*

## EXPERIMENTAL ASPECTS OF HYDROGEN ION CONCENTRATION

[ABSTRACT]

THE significance of hydrogen ion concentration for chemical changes of all kinds and for the most varied industrial and biological processes is patent to any one who glances at current scientific literature. The activity of enzymes, the efficient purification of water and the behaviour of clay in the potter's hands, to take only one or two examples, are alike dependent in a marked degree on this factor, whilst anything more than the slightest variation in the hydrogen ion concentration of the blood is incompatible with health.

An appreciation of these important facts starts from the obvious differences between solutions of strong and weak acids of the same total acidity. Equivalent solutions, for example,



of hydrochloric and acetic acids differ notably in freezing point, electrical conductivity, and influence on the rate of certain chemical reactions. These differences are determined mainly by the degree of ionisation, and in the case of a weak acid like acetic acid, a clear distinction can be drawn between "total" and "effective acidity," the latter quantity being measured by the hydrogen ion concentration  $[H^+]$ , and frequently expressed in terms of the so-called  $p_H$  value, where  $p_H = -\log_{10}[H^+]$ .

Besides the standard electrometric methods of determining hydrogen ion concentration, now being developed in the direction of continuous record and automatic control, the colorimetric method is found valuable in many cases. The fact that for different indicators the colour changes occur at quite different  $p_H$  values, and that the colour change in any particular case is not absolutely sharp but takes place gradually over a limited  $p_H$  range, underlies the practical use of the colorimetric method. It is assumed that two solutions which exhibit a colour match (for the same amount of indicator) have the same  $p_H$  value. In reality this principle is subject to some qualification.

A significant point that emerges from the study of hydrogen ion concentration is the extent to which the  $p_H$  value of a weak acid is altered by the addition of a neutral salt of the acid. Thus, if a little methyl red is added (i) to pure water, (ii) to sodium bicarbonate solution, and a current of carbon dioxide is then passed through both liquids, colour change occurs in the water but not in the bicarbonate solution.

Solutions which contain a weak acid in

presence of its neutral salt have, moreover, a remarkably steady  $p_H$  value, which is altered to a relatively slight extent by the addition of strong acid or alkali. Because of the resistance which they offer to change of acidity, mixtures of this kind are termed "buffer" solutions. They play an important part in the accurate determination of  $p_H$  values, and the "buffer" effect is of prime significance, for example, in the regulation of the hydrogen ion concentration of the blood.

[J. C. P.]

May 22, 1931

MAJOR CHARLES E. S. PHILLIPS, O.B.E., F.R.S.E.,  
F.Inst.P.,  
*Secretary and Vice-President, in the Chair*

SIR WILLIAM BRAGG, O.M., K.B.E., M.A.,  
D.Sc., F.R.S., M.R.I.  
*Fullerian Professor of Chemistry*

## X-RAY INVESTIGATION OF THE STRUCTURE OF LIQUIDS

### [ABSTRACT]

WHEN a pencil of X-rays is sent through a liquid behind which a photographic plate is placed, the image, when developed, shows not only a spot where the pencil has struck, but, in general, one or more circular rings surrounding the spot. The effect resembles the appearance of coronæ or haloes seen round the sun or moon or any bright source of light when viewed through a mist.

Of the optical haloes there are at least three kinds. The rainbow may be set down as one of them. Rainbow colours are due to refraction in the spherical drops, and are seen when the observer has his back to the sun. The strangely shaped haloes of the Arctic regions are due to floating crystals of ice. The third kind is represented by the corona so often seen round the moon at night. In the latter case, the sizes of the coloured rings depend on the sizes of the drops of water in the cloud or mist. The smaller the ring the larger the drop must be. The result is

readily explained on the famous principle of the Interference of Light, due to Thomas Young, who lectured at the Royal Institution at the beginning of the last century. Not only drops, but fine fibres give the same effect. Young devised an instrument which is called the "erionometer," in which the coloured rings or fringes observed when viewing a bright source through a little wisp of wool were used to determine the diameter of the wool fibre.

Sometimes the colour effects are very beautiful; the edges of clouds can be brilliantly iridescent, the display of colour depending on the thickness of the cloud and the size of the drops. Particularly splendid colour effects can be produced in the laboratory by means of artificial fogs.

The wave-length of the X-ray bears approximately the same proportion to the size of the molecule as the wave-length of light to the size of the water drop; and some of the rings on the photographic plate can be explained in the same way that the coronæ are explained. But there is undoubtedly more than that in the phenomenon. It appears that sometimes the rings are due to arrangements of the molecules of the liquid in ordered array, as in a crystal, but the arrangements are only fleeting and irregular, so that the sharp pictures obtained with X-rays when crystals are used are blurred when the crystal is melted and becomes liquid. It has not been possible, until the X-rays provided the means, to demonstrate in a direct manner this tendency to arrangement; it may now be possible to examine its nature and extent in various liquids. It is in all probability an effective factor in determining liquid properties.

[W. H. B.]

Friday, November 20, 1931

SIR ROBERT ROBERTSON, K.B.E., M.A., F.R.S.  
*Treasurer and Vice-President, in the Chair*

C. H. LANDER, C.B.E., D.Sc.  
*Professor of Mechanical Engineering, City and  
Guilds (Engineering) College, Imperial College  
of Science and Technology*

## OIL AND PETROL FROM COAL

GREAT BRITAIN has no considerable deposits of natural oil. In the hope of discovering hidden sources, extended surveys were made during and after the Great War, but nothing was revealed that gave any indication of yields exceeding a few tons of oil a day. In marked contrast to this oil deficiency are our vast reserves of bituminous coal. Probably some of the less scientific members of my audience have not realised the close chemical relationship there is between oil and coal, in spite of their apparent dissimilarity. All fuels consist essentially of carbon and hydrogen combined in different proportions. In oil, the proportion of hydrogen to carbon is higher than in coal ; further, oil contains less oxygen than coal. It is thus obvious that in order to turn coal into oil the

proportions of carbon, hydrogen, and oxygen must be suitably readjusted.

Various ways of doing this have suggested themselves to the scientific mind, but oil was first produced commercially from coal almost, as it were, accidentally, for it is one of the by-products in the manufacture of gas from coal.

Gas is made by the destructive distillation of coal, usually termed carbonisation. In this process, the coal is heated to a high temperature in closed retorts; the gas and condensable vapours which are driven off are collected, and from the resulting liquid products a certain quantity of oil can be prepared. In the course of these reactions there is a redistribution of the carbon and hydrogen atoms; the coke, which is left behind in the retort, consists mainly of carbon, and has a lower proportion of hydrogen than the original coal, while the liquid and gaseous products have a higher proportion of hydrogen than the original coal.

If the carbonisation is carried out at a lower temperature, say at a dull-red heat instead of the bright-white heat associated with normal gas-making processes, the yield of gas is less and the yields of coke and liquid products greater, while the latter are more nearly akin to natural petroleum. This process is usually known as low-temperature carbonisation.

## EXPERIMENT I

There has been set up on the lecture table an assay apparatus developed some years ago at the Fuel Research Station by Gray and King, following some preliminary work by Bone. The apparatus provides a method of obtaining accurate

information as to the quantity and quality of the resulting liquids and gases when carbonaceous materials are heated to different temperatures for different periods.

The complete lay-out of the Gray-King assay is shown in Fig. 1. About 20 grams of powdered coal are inserted in a glass or silica tube B, of 2 cm. diameter and 30 cm. long, closed at one

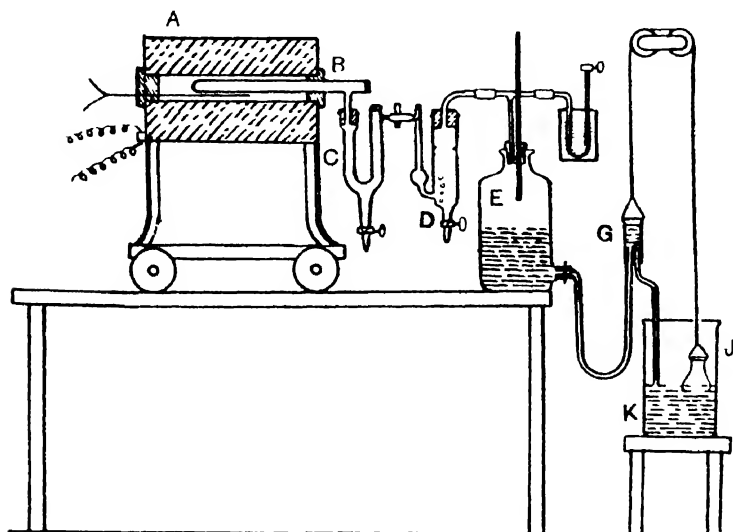


Fig. 1 --Gray-King Assay for the Low Temperature Carbonisation of Coal

end. At a distance of about 2 cms. from the open end a side tube 1 cm. in diameter is provided, which acts as an offtake pipe leading the gases into a condensing and scrubbing system. The silica retort is heated in the electric furnace A, while the U-tube C acts as a condenser and is provided with an extension piece for the reception of the liquid products. The tube D is filled with glass beads drenched with sulphuric acid for the

absorption of ammonia, and the gas is collected either over a mixture of glycerine and water, a solution of magnesium chloride in water, or water saturated with the gas obtained in a previous experiment. A constant pressure in the gas-holder is maintained by the ingenious apparatus shown at G, J, K. The gas entering the gas-holder E displaces liquid which flows into the receptacle G through a piece of india-rubber tubing. The overflow from G passes into the reservoir K, in which floats a counterpoise J. J and G are connected by a cord passing over the two pulleys shown. Thus, as the level in K rises, G is lowered ; and if E and K have equal cross-sectional areas a constant pressure is automatically maintained in the gasholder E. By an adjustment of the position of G at the beginning of the experiment, any desired difference of level can be steadily maintained throughout the test.

A, which may be either a gas or an electrical furnace, heats uniformly at least 6 inches of the tube B. The temperature is under control, and may be observed from time to time by means of a thermocouple in which the hot junction is in contact with the middle of the retort tube, as shown in the diagram.

The experiment will now be started, working at a temperature of about  $600^{\circ}$  C., and the low-temperature tar produced, which will be examined at a later stage of the lecture, will be collected in the condenser C.

Since light spirit is at the present time far more valuable than heavy oils, there have been introduced methods of again redistributing the molecules in the liquid products from the carbonisation of coal, so as to obtain higher yields of the



lighter spirit. During this process, which is known as cracking, a residue, which has been deprived of hydrogen, appears as coke. Cracking is also widely applied to the heavier fractions obtained in the distillation of petrol from natural oils.

But in obtaining petrol directly from the carbonisation of coal low-temperature carbonisation, cracking pushed to its limits, and the scrubbing of the gas to recover further small quantities of light spirit, have not up to the present been able to raise the total yield of motor spirit beyond 6 or 7 gallons per ton of raw coal. It must, however, not be forgotten that the primary object of carbonisation processes is the manufacture of coke and gas, and that light spirit, valuable as it may be per gallon, is still only a by-product.

The enormous importance of oil and petrol in modern civilisation has naturally focussed attention on the possibilities of re-shuffling the molecules in the coal in a way favourable to greater oil production ; but, as I have already pointed out, coal, as compared with oil, is deficient in hydrogen. The possibility therefore suggests itself of adding extra hydrogen to the coal substance in order to make up this deficiency, and then, by some means or other, inducing the molecules of the mixture to re-shuffle themselves into oil molecules. This has actually been accomplished, and for this success due credit must be paid to the work of Dr. Friedrich Bergius, at Mannheim, who was the first to liquefy coal by direct hydrogenation.

Important and striking developments of the hydrogenation process as applied to coal have been made during the past six years, in this country mainly by the Fuel Research Board and

Imperial Chemical Industries, Ltd. Fig. 2 \* shows how the oxygen, nitrogen, and sulphur in the coal are removed as water, ammonia, and sulphuretted hydrogen. The residual hydrocarbons in the coal (95 per cent. C, 5 per cent. H) break down and combine with hydrogen to give a large percentage of petrol (88 per cent. C, 12 per cent. H), the solid material probably passing through heavy oil (93 per cent. C, 7 per cent. H) and middle oil (91 per cent. C, 9 per cent. H). It will be seen that although at present petrol forms the most attractive product on account of its comparatively

CARBON	$\begin{matrix} \text{H}_2\text{O} & \text{NH}_3 \\ \text{H}_2 & \text{H}_2\text{S} \end{matrix}$		
	$\text{H}_2$	$\text{H}_2\text{S}$	
95	5	12	COAL
93	7	5	HEAVY OIL
91	9	3	MIDDLE OIL
88	12		PETROL

Fig

high price, the process could be stopped at an intermediate stage and so made to yield kerosene, diesel oil, or fuel oil.

So important to the interests of this country did the possibilities of the hydrogenation of coal appear that active work was inaugurated at the Fuel Research Station as early as 1922, with results so encouraging that in 1926 an intermediate-scale continuous plant, on the lines of Bergius' latest development, was set up at the Fuel Research Station, and, largely through the foresight of Dr. W. R. Ormandy, who had

\* For this, and Figs 5, 6 and 7, thanks are due to Imperial Chemical Industries, Ltd.

organised a syndicate to explore the possibility of applying the Bergius process to British coal, an agreement was entered into between the British Government and Dr. Bergius for the pooling and mutual discussion of the results obtained in both laboratories.

#### HYDROGENATION OF COAL. BERGIUS PROCESS

The Bergius process consists essentially in subjecting coal to the action of hydrogen at a high temperature and a high pressure. The powdered coal is prepared for treatment by mixing it with a small quantity of alkaline iron oxide (*luxmasse*), which acts as a catalyst, and a suitable oil or tar which may be a fraction of the liquid product obtained from previous runs.

For the preliminary exploration of the process on a small scale converters (Fig. 3) consisting of steel-walled vessels, closed by means of a blank flange, and of capacity about 2 litres, are used. A spindle projects from each end of the closed converter so that it can be carried on bearings and rotated over a row of gas flames. The pressure is measured by means of a gauge attached to one of the spindles through which there is drilled a passage to the interior of the vessel, and the temperature is measured by a thermocouple contained within a closed tube carried by the cover and projecting into the converter along its axis.

In hydrogenating coal by the original Bergius process, a thoroughly well-mixed paste is made from 20 parts of coal, 1 part of iron oxide (*luxmasse*), and 8 parts of oil, the oil being taken from some of the heavier fractions obtained from previous runs. This paste is inserted into the converter, which is then closed. Hydrogen is

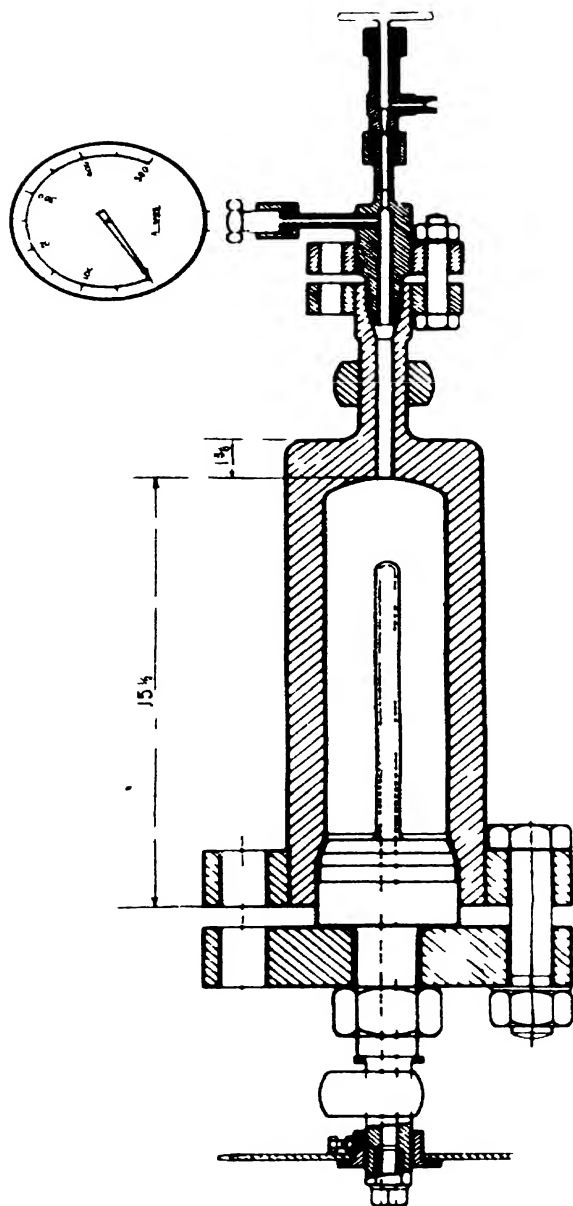


Fig 3 —Hydrogenation of Coal      Sectional arrangement of two-liter converter

pumped into the converter until a pressure of about 100 atm. is reached, when the converter is placed in its bearings and rotated over the gas flames, the temperature being raised to about  $450^{\circ}\text{C.}$ , while the pressure at the same time rises to about 200 atm. The reaction is allowed to proceed for two hours, after which the converter is cooled and the products extracted.

In these discontinuous experiments it is possible to use coal either in the dry powdered state or in a paste. In a continuous plant, however, there would be great difficulty in injecting a solid material in powdered form into an enclosure which is already under a high gaseous (hydrogen) pressure. By mixing the fine coal with oil into a paste a material is obtained which can be pumped, and this expedient formed one of the most important claims in the Bergius patents.

Fig. 4 shows the details of the small continuous Bergius plant, capable of dealing with about one ton a day, installed at the Fuel Research Station. The pump used for forcing the paste into the hydrogenation converters, which is shown at A, was specially designed to deal with a very thick material, say of the consistency of thick dough. Such a material when once in the cylinder can be forced into the converters against very high pressures, but will not follow up the piston during the suction stroke, where the head behind the paste is never greater than atmospheric; the pump is therefore filled during the suction stroke by means of a rotating worm. From the pump, the paste, which is kept agitated by mechanical stirrers, passes successively through three converters, C, D and E, which are surrounded by baths of molten lead; hydrogen of about 90 per



cent. purity is meanwhile also pumped at 200 atmospheres pressure into the converters by means of a four-stage compressor B. In this arrangement the first converter is used mainly as a heating chamber, the temperature being raised almost to that necessary for the hydrogenation re-action at this pressure. The second and third converters are maintained at the temperature which previous experiments have shown to give the best results for the particular type of coal under treatment. On completing its course through the converters, which takes about two hours, the hydrogenated product and surplus hydrogen are first cooled in the condensers F and then passed through a reducing valve G, which reduces their pressure to 60 atm. They are then allowed to separate in the separator H. From H the gas is taken to a scrubber, I, where, still at a pressure of 60 atm., it is scrubbed with oil in order to recover the light spirit. At periods of approximately one hour the liquids remaining in the separator H are blown down to the atmospheric separator K. Further gas is given off, which is passed to the gasholder. The liquid products collecting in K are periodically run off, either directly, or after centrifuging, to storage tanks.

The product removed from the plant is a relatively mobile oil, and the rough balance sheet of the process shows that 50 per cent. of the coal is transformed into distillable oil, 20 per cent. into gas, and about 15 per cent. remains as partially converted material. Some of the partially converted solids remain in suspension in a very fine state in the crude hydrogenated product, and make it very difficult to distil, but by taking proper precautions a series of fractions, as listed below,

can be obtained. The heavier fractions can be rehydrogenated for the production of a further quantity of light spirit.

A typical example of the yields per ton of coal obtained in the continuous plant (one ton per day) at the Fuel Research Station is given in Table 1.

TABLE 1  
YIELDS PER TON OF COAL FROM SMALL CONTINUOUS  
BERGIUS'S PLANT

Hydrogen consumed 114 lb		lb
Fraction]	0°-175°	83
"	175°-230°	208
,	230°-270°	197
,	270°-310°	105
,	310°-360°	208
Pitch		329
Gas benzene		42
Bergin gas		325
Unconverted coal		363
Water		179
Coal ash		161
Loss		154
		2 354

Reduced to the dry ash-free basis, the hydrogen consumed by 100 lb. of coal amounts to 5.7 per cent., and Table 2 shows how this hydrogen is distributed amongst the resulting products in the continuous Bergius process :

TABLE 2  
DISTRIBUTION OF HYDROGEN IN THE BERGIUS  
PROCESS

Hydrogen in 100 lb coal	5.6 {	11.3 lb.
Net hydrogen supplied	5.7 {	
HYDROGEN IN PRODUCTS		lb
In oils		5.3
In liquor		1.0
As $\text{CH}_4$ , etc		4.7
In residue		0.3
		—
		11.3



## HYDROGENATION OF COAL. FUEL RESEARCH STATION MODIFIED PROCESS

Further experimental work was carried out at the Fuel Research Station in order to increase the yield of the lighter fractions at the expense of the heavier oils, and to examine the process in the absence of a complicating factor such as a liquid vehicle for converting the coal into a paste. Improved catalysts were used, and the work carried out in two stages. In the first stage, coal mixed with a suitable catalyst was heated under pressure in a stream of hydrogen. The reaction products were carried over by the hydrogen and through a second catalyst in which further conversion to motor spirit took place in the gaseous phase. Experiments have been carried out using 50 lb. of clean coal, and a yield of 140 gals. of motor spirit was obtained per ton of dry, ash-free coal. The results are set out in Table 3, and a hydrogen balance for 100 lb. of coal substance (ash-free and dry) is worked out in Table 4. The net hydrogen required amounted to 8.8 per cent. by weight of the coal, giving, together with the 5.6 per cent. already present, a total of 14.4 per cent. of hydrogen required for the reactions, as shown in Table 5.

HYDROGENATION OF COAL  
FUEL RESEARCH STATION. MODIFIED PROCESS

TABLE 3

## YIELDS OF PRODUCTS

(1) *Liquid-Phase Reaction*

<i>Input</i>	lb.	<i>Output</i>	lb.
Coal, ash-free and dry . . . .	100	Crude oil . . . . .	64.6
Catalyst . . . . .	1	Gas spirit . . . . .	4.5
Net hydrogen . . . . .	2.3	Solid residue . . . . .	11.3
		Liquor . . . . .	8.7
		Gaseous hydrocarbons . . . . .	8.8
	<hr/> 103.3 <hr/>		<hr/> 97.9 <hr/>

(2) *Gas-Phase Reaction*

<i>Input</i>	lb.	<i>Output</i>	lb.
Oil and spirit . . . . .	69.1	Oil spirit, b.p. < 230° . . . . .	30.9
Net hydrogen . . . . .	6.5	Oil, b.p. ~ 230° . . . . .	5.5
		Gas spirit . . . . .	17.7
		Liquor . . . . .	5.2
		Gaseous hydrocarbons . . . . .	16.1
	<hr/> 75.6 <hr/>		<hr/> 75.4 <hr/>

<i>Composition of Spirits</i>	<i>Gas spirit</i>	<i>Oil spirit</i>
Aromatics . . . . .	25.6	23.3
Unsaturateds . . . . .	5.8	7.6
Saturateds . . . . .	68.6	69.1

HYDROGEN REQUIRED FOR A YIELD OF 154 GALS. OIL (140 GALS. SPIRIT)  
PER TON OF DRY, ASH-FREE COAL, EXCLUDING THE HYDROGEN OF  
THE COAL

	<i>Per cent. of coal</i>
Hydrogen in gaseous hydrocarbons produced . . . . .	5.9
„ in liquor (water and ammonia) produced . . . . .	1.4
„ in solid residue . . . . .	0.4
Gain of hydrogen in oil and spirit over that in the coal . . . . .	1.1
	<hr/> 8.8 <hr/>

∴ Net hydrogen required = 8.8 per cent. of coal  
= 35,300 cu. ft. per ton.

## F.R.S. HYDROGENATION OF COAL

TABLE 4

HYDROGEN BALANCE FOR 100 LB. OF DRY, ASH-FREE COAL

(1) *Liquid-Phase Reaction*

<i>Input of Hydrogen</i>		<i>Output of Hydrogen</i>	
	lb.		lb.
In coal . . . . .	5.6	In crude oil . . . . .	5.7
Net hydrogen . . . . .	2.3	„ gas spirit . . . . .	0.5
		„ solid residue . . . . .	0.4
		„ liquor . . . . .	0.9
		„ gaseous hydrocarbons . . . . .	0.4
	—		—
	7.9		7.9
	—		—

(2) *Gas-Phase Reaction*

<i>Input of Hydrogen</i>		<i>Output of Hydrogen</i>	
	lb.		lb.
In crude oil . . . . .	5.7	In oil product . . . . .	4.3
„ gas spirit . . . . .	0.5	„ gas spirit . . . . .	2.4
Net hydrogen . . . . .	6.5	„ liquor . . . . .	0.5
		„ gaseous hydrocarbons . . . . .	5.5
	—		—
	12.7		12.7
	—		—

## DISTRIBUTION OF HYDROGEN IN THE FUEL RESEARCH STATION

## MODIFIED HYDROGENATION PROCESS

TABLE 5

Hydrogen in 100 lb. coal . . . 5.6  
 Net hydrogen supplied . . . 8.8 } 14.4 lb.

*Hydrogen in Products*

	lb.
In oils . . . . .	6.7
In liquor . . . . .	1.4
As CH <sub>4</sub> , etc. . . . .	5.9
In residue . . . . .	0.4
	—
	14.4
	—

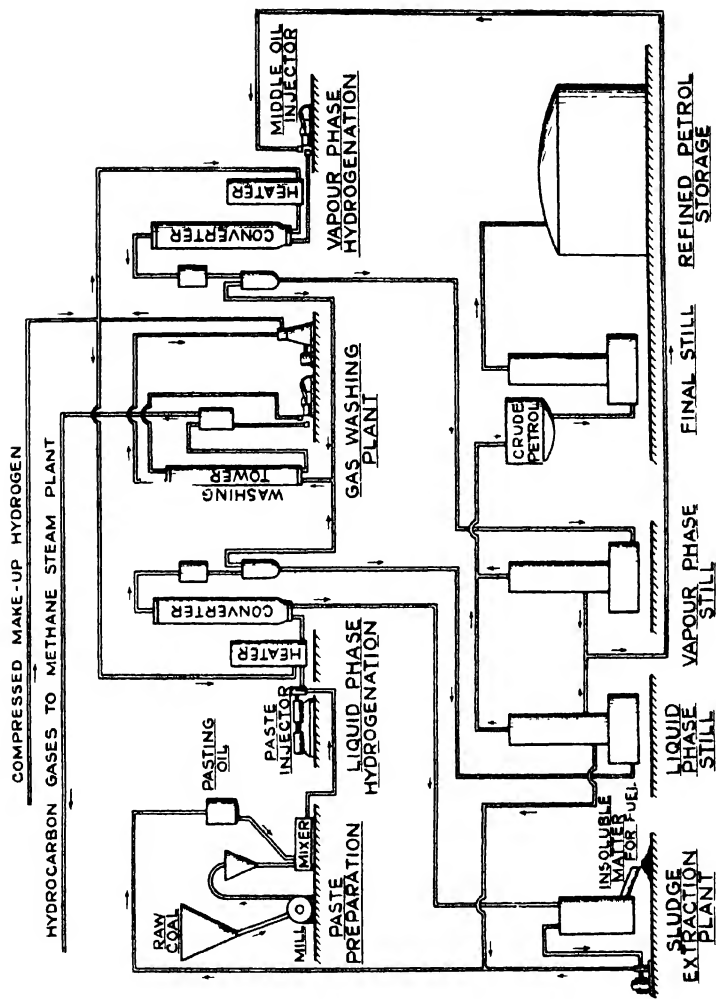
Table 6 compares the yields of the different products obtained in the processes of high- and low-temperature carbonisation and a hydrogenation process.

TABLE 6  
YIELDS FROM BITUMINOUS COALS WHEN SUBMITTED  
TO DIFFERENT TREATMENTS

	Carbonisation		Hydrogenation (Fuel Research Station)
	High tem- perature	Low tem- perature	
Motor spirit	1.1	1.1	45.1
Diesel oil and creosote oil	2.1	3.4	4.4
Fuel oil	0.5		
Lubricating oil		0.5	
Pitch	2.4	4.4	
Ammonia	0.2	0.1	0.5
Water	6.3	5.3	6.8
Gas	19.0	15.8	30.4
Organic matter insoluble in benzene			7.8
Coke	63.4	64.4	
Ash	5.0	5.0	5.0

Total

By 1927 the technical aspect of the hydrogenation of coal had reached so promising a stage that Imperial Chemical Industries, Ltd., thought it worth while to explore independently the possibility of its commercial exploitation, and for this purpose they set up a large research section at their Billingham factory where a full-scale plant capable of dealing with 10 or 15 tons of coal per day has since been developed. Fig. 5, which I have been able to reproduce by the kind per-



**FLOW DIAGRAM OF  
HYDROGENATION PLANT AND REFINERY**

Fig 5

mission of Imperial Chemical Industries, Ltd., shows the modified process as it is carried out at Billingham. The converters are now vertical, and are heated internally ; thus the serious difficulties caused in the earlier plant, by the action of hydrogen upon metals at high temperatures, have been obviated. The material passes into the converters at a fairly high temperature, and the heat of the reaction, which is exothermic, is more than sufficient to maintain the process. A relatively thin paste is used, which can be injected into the converter at a pressure of 200–250 atmospheres, where it is treated with hydrogen at a temperature of  $450^{\circ}\text{C}$ .

The hydrocarbon vapours, the volatile fractions of oil, the water, ammonia, etc., are carried away at the top of the converter in the stream of excess hydrogen. The liquid products are condensed under pressure, and the permanent gases are passed on for oil scrubbing, after which they are recirculated through the plant. The hydrocarbons scrubbed out of the gas are passed to a "methane-steam" plant for the production of hydrogen. The oils are distilled, and the heavier fractions used for pasting the coal. The petrol obtained requires only a slight purification treatment prior to use.

The intermediate oils are passed to a vapour-phase converter, where further hydrogen is added, and the mixture of hydrogen and oil vapours is passed over a catalyst ; a petrol is obtained from this vapour-phase hydrogenation product by distillation after reduction of pressure. The residual oil obtained in this phase may be re-cycled, or may be sold as diesel oil. The heavy oil residue from the first converter can be blown out, and

the liquid product recovered, the residue from which is a solid material containing ash, together with some 5 per cent. of the original coal ; it could be used only under the boilers. A diagram

### HYDROGENATION OF 1,000 TONS COAL

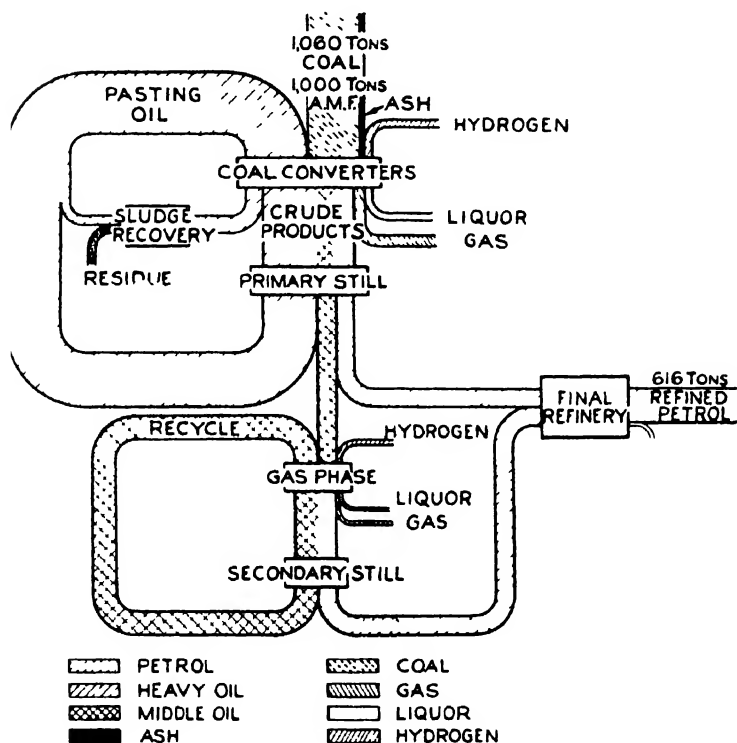


Fig. 6.

showing the ingoing and outgoing products in a plant designed for the hydrogenation of 1,000 tons of coal per day is shown in Fig. 6.

By re-cycling, etc., in the plant at the Fuel Research Station, some 140 gals. of motor spirit

per ton of coal as charged could be obtained, but this has been appreciably exceeded in the large-scale Billingham plant. In this, 100 tons of coal (reckoned on the dry, ash-free basis) is capable of yielding 62 tons (166 gals.) of petrol and 28 tons of gas, leaving a residue of about 6 tons of partially converted material. The gas can be used for hydrogen manufacture, and the residue for firing boilers.

For each ton of coal hydrogenated a further ton is required for raising steam for hydrogen manufacture and power generation, and for making the producer gas required for the process. The overall coal consumption is therefore 3.15 tons (reckoned dry and ash-free), or 3.65 tons of actual coal, per ton of petrol produced. The overall thermal efficiency is 43 per cent., as will be seen in Fig. 7.

The figures for cost given by Imperial Chemical Industries, Ltd., now work out at about 7*d.* a gal., of which 2*d.* is the cost of the coal. It will be seen that this petrol cost is actually less than the present duty, so that at the moment, in a plant of sufficient size, petrol from coal could compete very easily with petrol from foreign sources. Some time ago I was given an opportunity of examining both the technical and financial sides of the Billingham plant, and, although at that time so low a figure as 7*d.* a gal. had not been reached, it was already evident that 8*d.* or 9*d.* a gal. would not be exceeded.

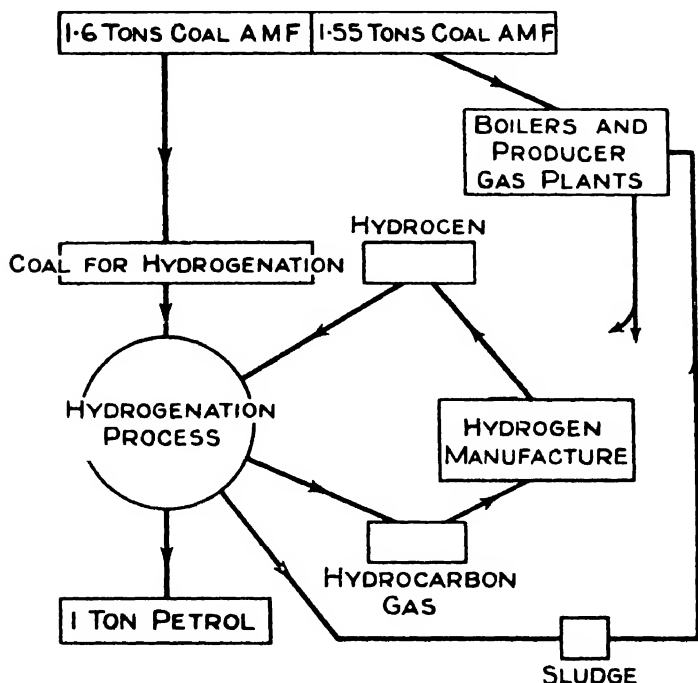
## HYDROGENATION OF TAR

The treatment of high- or low-temperature tar by hydrogenation is another method of pro-



ducing from home sources a supply of motor spirit. Work on this subject has been carried out

TOTAL COAL = 3.15 TONS ASH & MOISTURE FREE  
OR 3.65 TONS ACTUAL



NOTE :- THE AREAS ARE PROPORTIONAL TO THE HEAT VALUE OF THE MATERIALS.

Fig. 7.

by Ormandy and Varga, and at the Fuel Research Station. The Gas Light and Coke Co. are also investigating the method in order to find a more

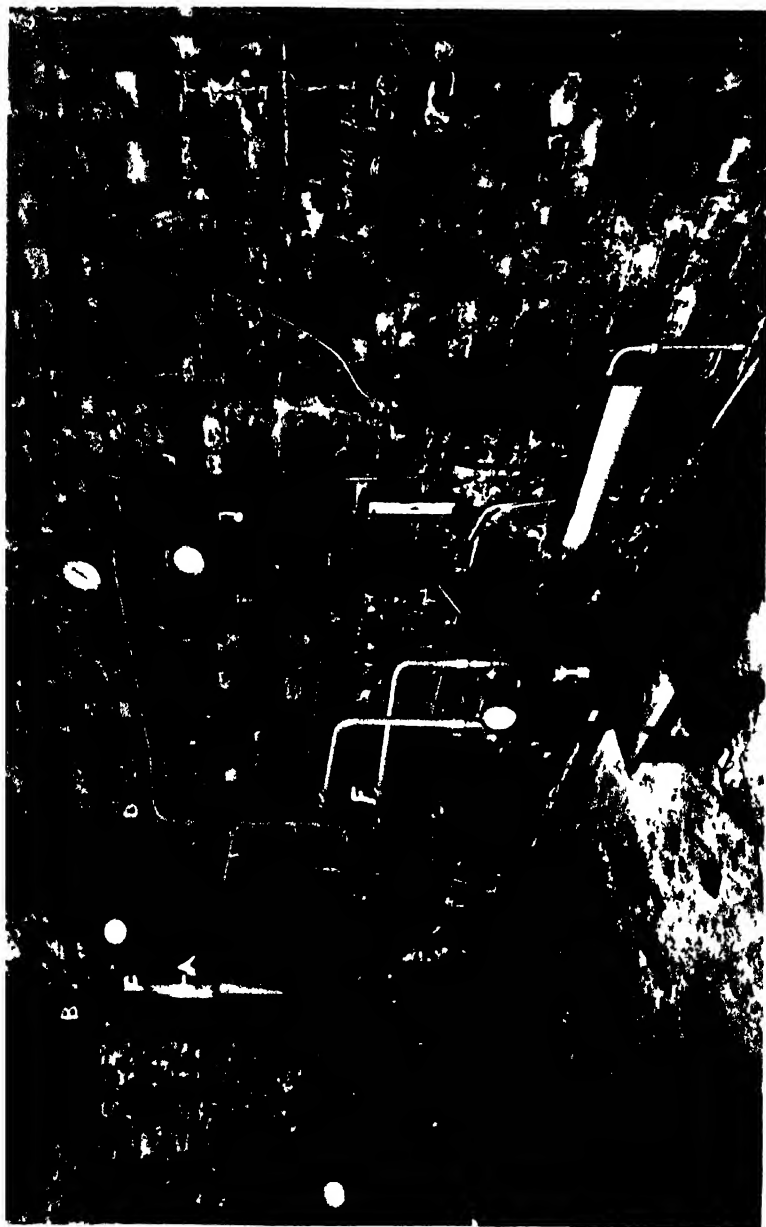


Fig 8 —Continuous tar hydrogenation plant at the Fuel Research Station.

favourable market for certain of their tar fractions which are at present almost a drug on the market. A small continuous plant for the hydrogenation of tar has been erected at the Fuel Research Station, and is shown in Fig. 8.

Tar is pumped at the rate of 1 kg. per hour into the converter A. At the position B it meets the hydrogen supply, and the two pass down the centre of the pipe to the bottom of A. In the lower third of the electrically heated converter is disposed a vessel containing a catalyst. From the surface of this catalyst an offtake pipe withdraws any heavy product through the bottom of the vessel. In the upper two-thirds is arranged a basket containing the vapour-phase catalyst. The vapours of the products leave the converter at the position C, pass through the condenser D to the collecting vessel E, where the pressure is reduced at short intervals of time to atmospheric pressure and the product run off. The gases released during this process pass through charcoal scrubbers, F, for the recovery of spirit.

The heavy product from the bottom of the converter amounts to about 10 per cent., and the light product to about 80 per cent. by weight of the tar charged.

The low-temperature tar obtained by carbonising coal at 700° C. with 10 per cent. steam has been treated in this plant. The results obtained by hydrogenation are given in Table 7. It will be seen that 150 gals. of motor spirit and 65 gals. of diesel oil were obtained per ton of low-temperature tar treated, whereas by straight distillation the corresponding figures would be 15 gals. of motor spirit, 117 gals. of heavier oils, and 884 lb. of pitch.

**TABLE 7**  
**HYDROGENATION OF LOW-TEMPERATURE TAR**  
**FUEL RESEARCH STATION PROCESS**

	kg		kg.
Tar (21 per cent tar acids)	100	Light product	80
Hydrogen	10	Heavy product	8
		Water	6
		Residual hydrogen	5
		Gaseous hydrocarbons	11
	-		-
	110		110
	--		-
Net hydrogen 5 kg			
or 20,000 cu ft per ton of tar			
Light product	SG 0.83		
Spirit — Distillate to 200° C		70 per cent by weight	
containing		2 per cent tar acids	
Refined spirit		38 aromatics	
		15 unsaturateds	
		47 saturateds	
Diesel oil		30 per cent by weight	
Heavy product	SG 0.93		
Yields per Ton of Tar			
Motor spirit		150 gals.	
Diesel oil		65 „	

## EXPERIMENT 2

Referring back to the carbonisation experiment which was started earlier in the lecture, it will be seen that the condenser tube now contains a quantity of fairly mobile low-temperature tar. A day or so ago some tar, similar in character with this, was hydrogenated at the Fuel Research Station. The converter has not been interfered with beyond relieving the pressure, so as to render it safe in transport. Let us now run off some of this hydrogenated product and leave it to distil in the apparatus before you.

At the same time, in a separate distillation apparatus, we will distil a similar product which has been obtained by direct hydrogenation of coal itself.

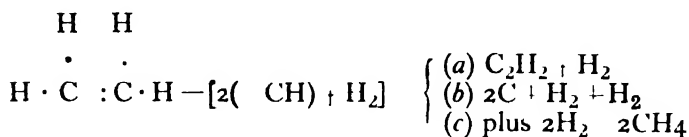
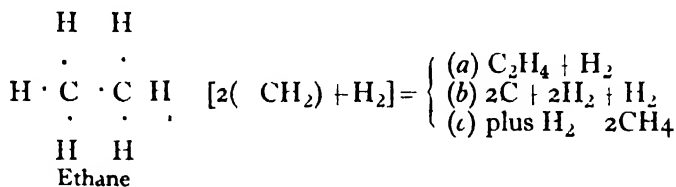
## MECHANISM OF THE HYDROGENATION REACTION

While distillation is proceeding we will consider for a moment the mechanism of the hydrogenation process. Much further experimental work will be needed to explain the precise effect of hydrogenation on the various constituents of coal, crude oil or tar, which are all very complex substances, but we already know that the hydrogenation action is a progressive one. When coal is subjected to hydrogenation, the first action is that it becomes plastic, and if hydrogenation is stopped at this stage a pitch-like material is obtained. If a non-coking coal is mildly hydrogenated, it is converted into a material possessing marked coking properties, and so we have presented to us for the first time the possibility of converting non-coking coal into coking coal, which, it must be admitted, is not at present an attractive commercial proposition.

An interesting paper describing investigations into the "Thermal Decomposition of Hydrocarbons," viz., methane, ethane, ethylene, and acetylene, was given by Bone and Coward to the Chemical Society in 1908.\* The character of the products formed when these gases were heated, either alone, or in the presence of hydrogen, was examined, and it was concluded that "in the cases of ethane and ethylene, it may be supposed that the *primary* effect of high temperature is to cause an elimination of hydrogen with a simultaneous loosening or dissolution of the bond between the carbon atoms, giving rise (in the event of dissolution) to residues such as :  $\text{CH}_2$  and  $\cdot \text{CH}$ .

\* "The Thermal Decomposition of Hydrocarbons," Bone and Coward *J C S* 1908, 93, 1197

These residues, which can only have a very fugitive separate existence, may subsequently either (a) form  $\text{H}_2\text{C} : \text{CH}_2$  and  $\text{HC} : \text{CH}$ , as the result of encounters with other similar residues ; or (b) break down directly into carbon and hydrogen ; or (c) be directly "hydrogenised" to methane in an atmosphere already rich in hydrogen. These three possibilities may all be realised simultaneously in the same decomposing gas in proportions dependent on the temperature, pressure, and amount of hydrogen present. The whole process may be represented by the following scheme, the dotted line indicating the tendency to dissolve the bond between the carbon atoms :



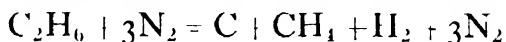
Ethylene

In one of his experiments Bone heated mixtures of ethane and nitrogen and ethane and hydrogen in a hot tube and maintained them at  $800^\circ \text{C}$ . for one hour, with the following result :

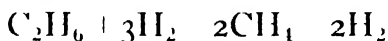
		Percentage methane obtained			Mean	
Original	$\text{C}_2\text{H}_6 + 3\text{N}_2$	18.5	17.15	18.3	18.7	18.15
Mixture	$\text{C}_2\text{H}_6 + 3\text{H}_2$	42.9	38.0	43.9	40.15	41.25

$$\text{Ratio } \frac{41.25}{18.15} - 2.27$$

From this it appears that with an inert gas the result corresponded very nearly with the equation

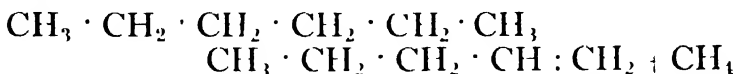


whereas with active hydrogen the change appears to be principally



In the latter equation the theoretical yield of methane is 50 per cent., whereas the actual amount obtained was 41.25 per cent., or 82.5 per cent. of the theoretical yield.

These and other experiments give a clue to the effect on a hydrocarbon molecule of a plain cracking treatment or a hydrogenation treatment. In the former treatment, using ethane, it will be seen that the methane produced is about 18 per cent., while hydrogenation gives about 41 per cent. of methane. Little work has been done on the cracking and hydrogenation of the more complex hydrocarbons in their pure state, but in 1896 Haber,\* using hexane, proved conclusively that between 600° C. and 800° C. the primary cracking took place by the elimination of methane and the formation of the lower olefine  $\text{C}_5\text{H}_{10}$  thus :



Haber regarded this action as typical of the behaviour of other bodies when subjected to cracking.

So far as I am aware, no experimental work has been done on the hydrogenation of hexane, but by analogy from the work of Bone it appears probable that if excess hydrogen had been present

\* Haber (*Ber* 29, 269), 1896.

in Haber's experiments some of the olefines would have been hydrogenated to pentane. This assumption is confirmed to some extent by the fact that in hydrogenating low-temperature tar and other heavy oils the separation of carbon can be practically eliminated, and the production of permanent gases lessened.

The above considerations, while admittedly incomplete, provide a useful picture of the reactions taking place during the hydrogenation of such substances as coal, oil, or tar.

### EXPERIMENT 3

Let us now turn to the distillation experiments. You will see that in both cases about a cupful of clear motor spirit has accumulated, and we will test this in the motor-car engine which has been brought here for the purpose. The engine responds immediately to the starter button, and continues to fire with regularity on either sample.

### SYNTHETIC PRODUCTION OF ALCOHOLS AND HYDROCARBONS FROM MIXTURES OF CARBON MON-OXIDE, AND HYDROGEN

It would be undesirable to conclude without touching shortly on the third possible method of producing motor spirit from coal, namely, the synthetic production of alcohols and hydrocarbons. Only in exceptional circumstances could this process compete with carbonisation or hydrogenation for the production of liquid fuels, but for the production of alcohol for solvents it has already become the basis of a large industry. The raw coal is first carbonised to produce coke, the liquid and gaseous products finding their normal



markets ; the coke is then subjected to the water-gas process so as to produce a mixture of carbon monoxide and hydrogen. By the use of various catalysts, together with, if necessary, additional hydrogen, liquids of various types are obtainable. Such catalytic conversion has been investigated in Germany by Fischer and the Badische Anilin und Soda Fabrik, in France by Patart and his co-workers, and in this country by Professor Morgan at the Chemical Research Laboratory, by Professor Bone at the Imperial College of Science and Technology, and by Imperial Chemical Industries Ltd.

#### EXPERIMENT 4

By the courtesy of Professor Bone and Dr. Newitt I am able to show you an experiment in which alcohol is obtained. The pressure bottle is filled with a mixed gas consisting of  $\text{CO} + 2\text{H}_2$  ;

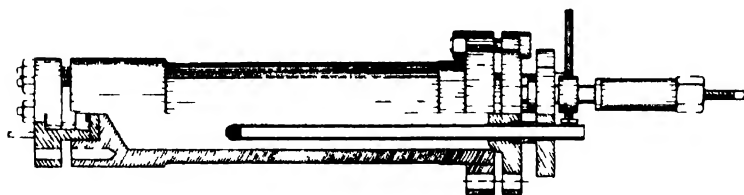
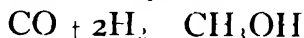


Fig. 9 — Professor Bone's pressure catalyst chamber for synthetic production of alcohols from carbon monoxide and hydrogen

this is passed into a catalyst chamber, Fig. 9, under 100 atm. pressure. The catalyst chamber is maintained at a temperature of  $300^{\circ}\text{C}$ . by means of an electric furnace. Under these conditions the system in equilibrium contains 10 atm. methyl alcohol, 60 atm. hydrogen, and 30 atm. carbon monoxide, and on cooling and

condensing out 4.4 gms. of methyl alcohol should be obtained.

The equilibrium constants for this reaction have formed the subject of experiment by Dr. D. M. Newitt, who in 1929 published before the Royal Society \* a paper giving the results of his work on the reversible system



Dr. Newitt employed both a static and a flow method, and in each case approached equilibrium from both sides, that is to say, from a system which consisted initially of the gases, and from a system which consisted initially of the alcohol. Various temperatures were used, and a remarkable agreement was obtained.

As an example of the importance of this work, Dr. Newitt's results show that at 200 atm. and 327° C. the partial pressures of the equilibrium of  $\text{CO} - 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$  mixtures would be

$\text{CO} = 54.5$ ,  $\text{H}_2 = 109.0$  and  $\text{CH}_3\text{OH} = 36.5$  atm.

Previous workers had deduced equilibrium constants by various theoretical means in which the partial pressure of methyl alcohol under the conditions referred to varied between 83 atm. and 168.5 atm. The divergence of the true partial pressure 36.5 from the above, illustrates how time and energy may be frittered away in searching for a more active catalyst in order to improve yields over the limit which has been set by Nature.

Dr. Franz Fischer of Mulheim has worked on the catalytic conversion of mixed gases at atmospheric pressures, and has produced liquid and solid hydrocarbons of the petroleum series. Oxygen-containing products are absent, and a

\* *Proc. Roy. Soc., A*, 1929, 123, 336

yield of 100 gms. of solid, liquid and liquefiable hydrocarbons is claimed from each cubic meter of water gas.

From this brief description of some very complicated processes it will be seen that on the technical side much has been achieved. By the carbonisation of coal, liquid products suitable for use in internal combustion engines or in furnaces can be obtained directly, but not in large quantities compared with the amount of coal used ; in such processes the greatest stress must be laid upon the markets for the solid and gaseous products, oil and petrol being merely by-products. By the hydrogenation of petroleum, or of low-temperature tar and certain fractions of high-temperature tar, large percentage yields of motor spirits can be obtained.

By the direct hydrogenation of a suitable coal some 160 gals. of motor spirit per ton of coal treated can be made, and even when the additional coal for the process is taken into account the yield is 80 gals., and the thermal efficiency is 43 per cent. Alternatively, motor spirit can be obtained synthetically either in the form of alcohols or of hydrocarbons, by first converting the coal into carbon monoxide and hydrogen, but not, under present conditions, so cheaply as by hydrogenation.

I think most of you will agree that in view of the mechanical difficulties of working, on a large scale, a process involving simultaneously high pressures and high temperatures, the technical progress of coal hydrogenation has been surprisingly rapid. It is now undoubtedly possible to manufacture petrol from coal. The commercial prospects of the process are nevertheless uncertain, for it is always difficult to forecast the future

of a synthetic, in competition with a natural, product.

Five or six years ago petrol was much dearer than it is now, and such a hydrogenation process as that developed by Imperial Chemical Industries, Ltd., would have been able to show a substantial profit ; but at the low prices now ruling the process has little prospect of paying its way, unless a big enough import duty is maintained.

It would have been impossible, particularly on the experimental side, to prepare this lecture without much willing assistance. In particular, I wish to express my thanks to Dr. Sinnatt, Dr. King, and Mr. Edgcombe of the Fuel Research Station, who have supplied and worked the experimental apparatus for the production of motor spirit from coal and tar, and to Professor Bone, Dr. Newitt, and Mr. Allum for enabling me to show you how alcohol can be produced from mixtures of carbon monoxide and hydrogen.

[C. H. L.]

Friday, December 4, 1931

SIR ROBERT HADFIELD, Bart., J.P., D.Sc., F.R.S.  
*Manager, in the Chair*

G. P. THOMSON, M.A., F.R.S., M.R.I.  
*Professor of Physics in the Imperial College of  
Science and Technology*

## THE OPTICS OF ELECTRONS

ALMOST all progress in physics has come from comparing the unfamiliar with the familiar. One could hardly have a better example than the story of Newton's apple for this comparison assimilated the motion of the moon to the motion of a falling body. The great essential is to use an idea with which one is already familiar. It is less important that the idea should be really understood, if indeed anything in the physical world ever can be understood in any absolute sense. The falling of the apple was not understood then (one may perhaps doubt if we understand it much better now, when we say that it is a consequence of the curvature of space), but it was at least familiar, and the mind needs familiar images with which to work. Now in the study of the very small there are two pictures which have proved their use. One is as old as the Greeks, the idea of a particle, hard, small, smooth, an idealised

grain of sand. Generally it is pictured as moving, and the universe as an endless game of snooker with every ball played at once. The other view is only seven years old, but it is a promising youngster, and in the last few years has come to take an equal place with its elder brother, so producing a curious duality in our views of matter.

I refer to the idea of matter as waves, which was invented by Prince Louis de Broglie. Now light has long been regarded as waves, and to many physicists, at least, waves of light are more familiar in their properties than the more tangible waves of water or of sound. To-night I hope to show first that this analogy between matter and light is a good one, and then to point out where it fails, for, of course, no analogy is perfect.

According to de Broglie any piece of matter should have wave properties, but in most cases the wave-length would be too small to detect; even with the most refined experiments. The heavier the piece of matter and the faster it is moving, the shorter is the wave-length, and although recently the wave properties of atoms as a whole have been detected, most of the experimental work has been done with the lightest known pieces of matter, namely, electrons. Even with these, the wave-length is usually much less than that of light. Thus for the electrons used in the experiments I hope to show you to-night, which form part of a beam of cathode rays from a discharge in rarefied air, the wave-length is usually about  $\frac{1}{40}$  of the size of an average atom, and only about  $\frac{1}{100,000}$  of the wave-length of red light. Actually, if the voltage is 30,000 volts, the wave-length is about  $7 \times 10^{-10}$ .

The characteristic feature of those waves which one can actually see and feel is the periodic motion of the water or other medium, but when one comes to waves in which one can no longer actually see the medium bobbing up and down, the most characteristic wave property is that called "interference." This is the property by which, for example, two beams of light can produce darkness, and is explained at once as due to the superposition of two trains of waves in such a way that the crest of one wave neutralises the trough of another. In the case of light this leads to a pattern of light and dark bands whose sharpness may be much increased by using not two waves only, but a large number of wavelets produced by the scattering of a single wave from a number of obstacles arranged in a regular order. To get a satisfactory pattern the distance apart of the scattering objects must not be too great compared with the wave-length of the light. This led Laue to use the atoms of a crystal as scattering centres to measure the very short wave-length of X-rays. The use of a crystal, however, introduces a complication, for we are not only concerned with the wavelets from one plane of atoms, but with those from successive planes. The result is that only if the crystal is correctly adjusted to the incident beam will there be a strong beam selected by interference. If the crystal is powdered, and the pieces are arranged at random in the path of the rays, there will always be some pieces correctly adjusted, and the beams from them will lie on cones and their intersection with a screen will show as rings. The absolute sizes of the rings are proportional to the wave-length and inversely, as the spacing of the atoms, while the relative sizes

of the different rings in any one experiment depend on the arrangement of the atoms in the crystal.

Now electrons are certainly scattered by atoms. If they are like waves they should give interference, and the scattered waves should be concentrated in certain directions; presumably the electrons will show themselves most where the waves are concentrated. In my early experiments this was done by passing a narrow beam of cathode rays through a thin foil and receiving the scattered rays on a photographic plate. When developed these plates showed ring patterns which were in agreement with those calculated from de Broglie's theory and the known crystal structure of the metal films used. To get good results the films had to be of the order of  $10^{-6}$  cms., and this limits the substances with which one can work. I have found, however, that equally good results can be got by reflecting the rays from a block of material whose face has been suitably prepared. It is probable that the rays pass through minute projections on the surface, so that the reflection is really only apparent. In this way ring patterns have been obtained with a variety of substances such, for example, as spluttered metals and metals, which have undergone surface oxidation or other chemical change. The method enables one to examine a very thin layer of the substance, for the effective depth of penetration is of the order  $10^{-6}$ . It appears that almost any surface will give some kind of a pattern providing that it is reasonably flat.

The concentration due to interference is, as we have seen, much more marked if there are many scattering centres arranged in order. This is so in the case of the above experiments, for



though the crystals are small enough to be very numerous, even in a small piece of material, they each contain a very large number of atoms. Recently Wierl has made experiments of the same character, but with gases. Here the scattering particles are the atoms, of which there are only a few in each molecule, so though rings are formed they are not very sharp. Nevertheless, the theory holds, and Wierl has calculated the distance apart of the atoms in various molecules from the sizes of the rings. He has been able to draw a number of interesting conclusions about the relative positions of the atoms in the molecules. For instance, he finds that the carbon atoms in the benzene rings lie in a plane.

The apparatus I have described will also serve for single crystals. Here, however, we should expect nothing unless the crystal were suitably adjusted, and then only a small number of spots. With a cleaved surface of rock salt these expectations are approximately fulfilled, though there is enough latitude from various causes for some sort of a spot to appear for almost any setting of the crystal. In addition, there appear a number of black and white lines which have been ably explained by the discoverer, Kikuchi, as due to double scattering.

Some experiments with single crystals of metals have led to rather surprising results. When cut so that the face is crystallographically a simple one, these crystals give an extended pattern of spots of a very regular character. The pattern is just what we expect from a single layer of atoms arranged in the crystal form and set normal to the rays. The agreement is exact and extends to small details. The pattern is the polar reciprocal

of the atomic arrangement known to exist in the crystal, each spot of the pattern corresponds to a line of atoms in the crystal, and the whole plane of atoms behaves like two crossed optical gratings. Clearly, however, a single plane of atoms sticking out at right angles to the main surface is a mechanical impossibility. The surface was actually prepared by etching and was probably covered with pits and pyramids, through which the electrons pass. The reason for the extended pattern is that the thickness in the path of the rays is so small that the successive layers of atoms are not badly out of step over a considerable range of angle. This approximate agreement is helped by the small angle through which the rays are turned.

Some recent work in conjunction with Mr. Stuart on spluttered platinum films has shown that while the usual structure is that of normal platinum, abnormal types sometimes occur. One of these gives a pattern of straight lines, which is unstable and disappears under the action of the rays. It appears to be due to the presence on the surface of small pieces of some crystalline structure in which the atoms are arranged accurately in layers parallel to the surface, but each separate layer is largely chaotic. We have not been able to determine whether the atoms are those of platinum or of a gas. Another abnormal structure shows the presence of extra rings which may be associated with catalytic activity of the platinum.

While these experiments show the close resemblance between the behaviour of the electrons, and that of light in those experiments which were the original proof of its wave character, yet all the same one must not entirely abandon the particle idea. When the electron reaches the photo-

graphic plate it seems to forget that it is a wave and becomes a particle. If the plate were examined under a high magnification the pattern would show up as a number of black specks, each corresponding to one grain of silver bromide made developable. Each electron affects one grain only. Yet the waves which interfere must have been scattered from atoms over a wide front, and the sharpness of the ring and spots show that there has been a long train of waves acting, just as a sharp line in an optical spectrum implies a long train of coherent waves.

On the wave side of its nature the electron is a widely extended entity which in a sense occupies the whole region in which it might be found. An electron is like an able guerrilla leader who occupies a wide area with rumours of his presence, but when he strikes, he strikes with his whole force. No analogy is perfect, and though the analogy between light and electrons even extends to this curious duality of wave and particle, it breaks down in the end. Electrons are essentially different from light. They are acted on by electric and magnetic forces, and react on the bodies which cause these forces. Light does not, it only affects matter when it actually hits it; there is no action at a distance. Further, the electronic waves are a trifle less real than those of light. No one, it is true, has ever actually observed the frequency of visible light, but that of very long wireless waves can be directly followed and the difference must be only one of degree. Now as far as we know at present the *frequency* of electron waves is quite unobservable; it is always the *wave-length* which we find. Possibly one could observe differences of frequency under

very special conditions, but the absolute values seem to have no significance except as mathematical symbols. Different values can be assigned to this frequency and the calculated results still agree with experiment. Again, the fluctuating quantities or "displacements" in the light wave have a definite physical meaning, namely, electric and magnetic intensities. No one has observed the corresponding quantity in the electronic wave. Indeed, in the most successful forms of the theory it is not even a real number. Only the intensity of the wave has a physical meaning, namely, the chance that an electron will appear at the place in question. The two views of electrons, as particle and as wave, are parables, each enshrining a part of the truth. Whether between them they include all that we need to know, as some physicists believe, or whether there are not other aspects still undreamed of, is for the future to decide.

[G. P. T.]

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A. CHASTON CHAPMAN, F.R.S.  
*Manager, in the Chair*

C. G. DARWIN, M.C., M.A., F.R.S.  
*Tait Professor of Natural Philosophy in the  
University of Edinburgh*

## THE UNCERTAINTY PRINCIPLE IN MODERN PHYSICS

IN the course of the last twenty years there has grown up a great body of doctrine, the quantum theory, and its history is in some ways the most curious in the whole of science. The developments of our knowledge have often progressed in an uneven and irregular manner, with important ideas sometimes long overdue before they appear, but at least the progression is usually based on rational assumptions. With the quantum theory this was not so; from its very inception it seemed to run contrary to all logic. Many conservative physicists at first frankly thought that such a self-contradictory theory must be erroneous, but as more and more phenomena were accommodated it became impossible to doubt but that there was method in the quantum's madness, and it was possible to anticipate that some time a new synthesis would be made which would remove the contradictions and restore our reason to us. In 1925 the new synthesis was found, and this independently in two quite separate ways.

As would be expected, at first the new theory was very abstract ; it was, in fact, by denying the validity of the ordinary laws of multiplication that Heisenberg first brought logic into the old confusion, but it was only a couple of years later that Heisenberg himself showed how these rather formal methods would fit into our ordinary processes of thoughts in a natural way. It is with this aspect of the question that I shall be concerned, and in explaining it I shall make more use of the second resolution of the difficulties of the old quantum theory, which was started by de Broglie and worked out by Schrödinger. A great deal of what I shall be saying is to be attributed to Bohr, who more than any other has cleared up the difficulties in which the old theory was involved.

It is evidently out of the question for me to expound all the difficulties of the old quantum theory and then to set them right to do so would take many weeks. I propose instead to select two experiments, which between them typify the apparent contradictions of the theory, and then to show how the new principle, the Uncertainty Principle, removes the apparent contradictions. My experiments are to be regarded as types, each standing for a great mass of knowledge, and the reconciliation of them carries with it the removal of the main difficulties in the way of our understanding of the quantum theory.

My first experiment is simple, and in one form or another has been done again and again during the last thirty-five years. Take an evacuated tube arranged to carry an electric discharge between a pair of terminals. Cover one part of the glass inside with some powder of a mineral

called willemite, and observe what happens in the dark. We should see that the willemite emits faint sparks at intervals all over its surface. A more detailed study shows that each of the sparks is caused by the impact of an electron. An electron is a particle of electricity and is the lightest thing known ; it was by experiments of this type that its characteristics, mass and electric charge, were measured. Moreover the speed of the electrons could be measured in a variety of ways ; in some of the experiments it was done by opening and shutting two holes through which the electrons must pass in succession, and timing how long they took between them. To give a general idea of the speed, it is found that when there are 30,000 volts on the tube (not at all a high voltage) the speed is one-third of the speed of light. This experiment tells us quite unambiguously that an electric discharge is like a machine-gun firing bullets, the electrons, at a target.

Now turn to the second experiment. I ought, perhaps, to begin by confessing that this experiment has never been done ; as I describe it, you will see why it is not practically possible to do it. It is to be regarded as a type-experiment, containing the essential point of other experiments which are practical, such as the great experiment of Davisson, which first established the point I am about to explain. We shall again study an electric discharge of 30,000 volts in a vacuum, but this time with a different outfit inside. We place a shutter in the track of the electrons, containing two small holes in it close together. This is where the practical difficulty comes in, for the two holes are each to be only a thousand millionth

of a centimetre in diameter, and they are to be a hundred millionth of a centimetre apart. The tube itself is to be a metre long, and at the end of it, beyond the shutter, we place a photographic plate of extreme sensitivity. After a long exposure (probably centuries would be necessary) we develop the plate. If all this were practically possible there is no doubt what we should observe. The plate would be crossed by alternate bands where it was fogged by the electrons, and bands in between where it was blank, showing that no electrons came there. The bands would be about 7 cms. apart. This is the first half of the experiment. Now repeat it again, but this time with one of the two little holes blocked up. When this plate is developed, we shall find no bands at all, but a uniform fogging all over the plate. Now this is an extremely remarkable fact, when we try to understand how it could come about. Consider one of the blank places on the plate in the first part of the experiment. No electrons came there, and we might try and explain this by saying that in some way the place was protected from the electrons by the shutter. But block up one hole and the place is no longer protected. The addition of what ought obviously to be a further protection has, in fact, had the opposite effect. It is as though the victim of a detective story were invulnerable when sitting in his chair, no matter how many assassins are shooting into the room, as long as he keeps both windows uncurtained, but as soon as the blinds are drawn on one window he falls a victim to the next bullet. This is, of course, fantastic, but it is not more fantastic than my two experiments appear to be at first sight.



As I have stated it, this result seems very remarkable, yet it is a phenomenon quite familiar to any one who has studied physics. It is cognate to one of the great classical experiments of history, the experiment of Thomas Young with light. Young sent light through two small holes close together (though of course by no means so small or close together as those of our experiment), and observed the actual formation of bands, in much the way I described. He deduced from this that light must be a wave motion, and we must turn aside now to consider what this means.

It will suffice for us to take an example, and the most familiar of all will do, that of waves travelling on the surface of the sea. Imagine that we have a perfectly regular train of waves, crest following crest at regular intervals, advancing across the sea towards a breakwater. First suppose that there is a small gap in the breakwater, and consider what will happen on the other side. Evidently there will emerge from the gap a train of semicircular waves, with crests all at the same distance apart as before. Next suppose that we have two gaps in the wall not very far apart. To see what happens I will invoke a very fundamental principle in all wave motions, the principle of superposition, which declares that if there are two motions either of which could happen by itself, then there is a third possible motion of the water, which is simply the sum of the other two ; each motion goes on just as though the other were not there. In our case, then, semicircular waves will emerge from each gap, and these are to be superposed. It can be seen that at some places they reinforce one another, but at others they cancel out. This is the phenomenon of

interference, and is the explanation of Young's experiment with light.

Our experiment with the electrons has told us that electrons also can show interference, and we conclude that an electron is at any rate sometimes a wave. It is a natural question to ask what sort of wave it may be ; for example, the waves we have discussed were waves of the surface of water, sound waves are waves of compression of air, and so on. The answer can best be made by considering the case of light waves. It was natural for Young and the physicists of his time to ask what sort of medium carried the light waves of which he had established the existence, and a special name, the æther, was invented for this medium. But things are not helped on a great deal by the use of this name, since there is one essential difference between the æther and the media carrying sound waves, etc. We can do experiments with water or air which show us that they have properties unconnected with the waves they sometimes carry, but the only property of the æther is that it carries the waves of light. Consequently it is not much use talking about it except in connection with conveyance of waves, and so it becomes really a grammatical construction rather than a physical entity. The same is true for our electron waves, and, in fact, no one has felt the need of a name for the medium carrying them.

We have now got from our two experiments two very different pictures of the electron, in the first as a bullet, and in the second as a wave motion. We cannot see any resemblance between these pictures, and it is our chief aim to-day to see how they can be reconciled. One attempt at

reconciliation has been tried several times, but must be condemned altogether. If the electron is sometimes like a piece of grit and sometimes like a stormy sea, the natural compromise is to say that it is really a piece of grit floating in a stormy sea. This is no use at all; like many other compromises it enjoys all the disadvantages of both sides. It is not something in the sea that we need, it is the wave motion of the sea itself.

In order to see how we must proceed, we will first strengthen the contrast by uniting our two experiments into one. In order to do this we replace the photographic plate of the second experiment by a willemite screen. We should then observe that there were scintillations in the places where the photographic plate was blackened, but none at all in the blank spaces. We can describe what has happened shortly by saying that the electron behaved like a wave in going through the two holes, but changed over into being a bullet when it reached the screen. This is a very unsatisfactory account of the matter, because it attributes foresight to the electron as to what is expected of it, and if we are fanciful we can imagine that we could swindle the electron by painting the two holes so as to look like a willemite screen, and so cause it to be a particle when it ought to be a wave, and absurdities of that kind.

The answer to these contradictions was found by Bohr. It consists in recognising that experiments that evoke wave characters and those that evoke particle characters are always mutually exclusive, so that the contradictions do not exist in fact; we cannot ever deceive the electron by making the two holes look like willemite.

For take our experiment with the two holes ; this experiment verifies the electron's wave character. We will try to test whether the electrons were particles at the same time, and the best way of doing this would be to decide which of the two holes each single electron went through. To do this we put thin films over the holes, each lightly powdered with willemite ; then when an electron goes through a hole there will be a scintillation there, and in this way we can decide through which hole each electron went. We have thus verified the particle character of the electron, and so we now go round behind the screen to verify that the wave character is still all right, but when we do this we are distressed to find that there is no trace of the bands on the plate. A little thought, however, shows that this is natural, for the flashing of the willemite on the hole will certainly cause a reaction on the electron, altering its speed a little (or perhaps only its phase), and this is enough to spoil all chance of interference. Any experiment devised to show the particle character automatically debars us from verifying at the same time the wave character, and *vice versa*. The real point of Bohr's argument is that we now see that this is not a highly abstract doctrine, but almost a matter of plain common sense.

We have got to convince ourselves that the example cited is not exceptional, and that there is no case where we should find a conflict between the demands of the electron that it is to be either a wave or a particle according to the experiment to which it is submitted. But it will be best for the moment to assume this and to construct a view of nature which will enable us to think

about the way things behave. The best view, I think one might say the only view, that one can adopt is that there is in nature a fundamental duality, typified by the characters of wave and particle. An electron, and, in fact, any other piece of matter too, is a wave and a particle, and both characters must be kept in mind, but they must not be mixed. Some experiments evoke the particle characteristics, such as striking the willemite, and others the wave character; and whichever type of experiment is carried out it is this experiment that brings into prominence the corresponding character. We shall have to see later how it is possible that there is no contradiction in such ideas, but first we had better examine the nature of the duality itself, for it is something quite new in scientific thought. I think it should be admitted frankly that we were all quite happy before the duality was discovered, and that it would have been a simpler world if it had turned out that we did not need it, but there it is as the only way in which one can understand the fundamental difficulties of atomic theory. There is nothing like this duality anywhere else in science, but it may perhaps make it more acceptable if I recall that there is a duality in metaphysics which we all accept cheerfully and without complaint. I refer to the duality between the objective and the subjective, between, for example, the rather difficult abstractions of the scientific conception of heat and the much more poignant ideas we have when we burn a finger. Or, again, there is a very complete separation between the idea of light of wave-length one-twenty-thousandth of a centimetre, and the perception of green light, and yet the one always

causes the other. There is the same sort of interdependence, associated with the use of two entirely different languages, in the particle and wave aspects of the electron. It should, perhaps, be confessed that the analogy which I have drawn is not a close one, for the conceptions of metaphysics are not comparable to those of science, but nevertheless it is perhaps helpful as showing how completely and spontaneously we accept, and cannot help accepting, one duality, and so perhaps it may mitigate our difficulty in accepting another.

We must now see how the characters of wave and particle are to be associated with one another. The main character of a wave is the wave-length, the distance between successive crests. On the other hand, the main characters of a particle are its speed and position. There is a very simple relation between the speed of the particle aspect and the wave-length of the wave aspect; they are inversely proportional, so that the slower the electron the longer the wave-length. For our 30,000 volt electrons the wave-length, as calculated from the breadth of the fringes, will be very small, less than a thousand-millionth of a centimetre. This is for electrons with speed a third that of light, and it is mostly with these high speeds that the theory has been tested, since only so have the electrons enough energy to fog the plate or produce scintillations. But if we have much slower electrons we get longer wave-lengths; for example, an electron going at the rather slow rate of 1 cm. a second has wave-length about 7 cms.

This is the formal relationship, and I am not, of course, asserting that one could see a wave with crests 7 cms. apart under any conditions. What

is asserted is, that one would find an exact geometrical similarity between our experiment of the two holes and an experiment with ripples 7 cms. long on the surface of water; if these went through two gaps at the same distance apart the disturbed regions would be found at the same positions as those where the electrons appear. But now let us take our connections of the two aspects more literally. A wave of 7 cms. wavelength does not by any means imply two crests 7 cms. apart; it means a regular train of waves with crests spaced at 7 cms. intervals stretching to infinity in both directions. We have seen that such a wave system corresponds to a particle moving at a rate of 1 cm. a second, but that gives no information at all about what is the most natural and reasonable question that we may ask—where in all this wide sea is the particle? It was the finding of the answer to this question that cleared the whole business up. The answer is that it may be absolutely anywhere. This was quite unforeseen, and seems at first sight contrary to common sense—for, after all, the electron must be somewhere, and there ought to be something corresponding to this fact in the wave aspect. It is the fact that it does make sense that is the point of the Uncertainty Principle.

To understand it, let us take a slightly different case, since a wave motion stretching to infinity is rather overwhelming. Take the case of a "wave packet" composed of a number of crests at equal intervals, surrounded by quiet water. If this represents an electron wave, where is the electron-particle? The answer is that though we cannot say where it is, we can say where it is not, for it cannot be in the undisturbed region

outside the packet ; if the idea of waves is to mean anything, we must at least suppose that where there is no wave disturbance there can be nothing happening, and so no particle. We must next make a digression to consider how such a wave packet will behave with the lapse of time ; this is a well-known and much-studied question of wave motions in general. It is found that a patch of waves travels along in a straight line at a definite rate depending on the wave-length, but that as it goes it spreads so as to increase slowly in size. The rate at which it spreads depends on the length of the packet ; a long packet, containing many crests, will only spread slowly, while if it only has a few its spread is very rapid. For our electron we are supposing that the particle is certainly at first somewhere in the packet ; where is it later ? Evidently still in the packet, so it must have travelled with the speed of the packet. But here comes an important point ; the particle's speed cannot be fixed accurately in this way, because the packet is spreading. Thus if we imagine that the particle was moving at the head of the packet it would be going faster than if it were at the tail ; and it would be going still faster if it started at the tail and ended at the head. So our idea that the particle may be anywhere in the packet carries with it the implication that the speed is to some extent indefinite. In this way we see that our idea of duality will only work on the condition that there is some indefiniteness in the position and speed of the particle.

The indeterminacy can be expressed in a more definite form. Thus in a very long wave packet the position of the electron is very uncertain, but as such a packet does not spread much the speed



is rather precise ; on the other hand, a short wave packet will clearly define a rather accurate position for the electron, but such a packet spreads very quickly, and this implies great uncertainty in the speed. It is possible to give rough numerical limits to the two uncertainties ; suppose that we measure position in centimetres and speed in centimetres per second, then it happens by a sort of numerical accident that for electrons the product of the two uncertainties is about 1. For example, if I know for sure that an electron is somewhere within a distance of a hundredth of a centimetre from some place, then the Uncertainty Principle asserts that its speed must be uncertain to about a hundred centimetres a second, so that it would only stay for sure in the region where I had located it for a ten-thousandth of a second. At first sight this seemed a fantastic result, and it is little wonder that it was only recently discovered that it is entirely sensible and natural.

In order to justify our dualistic hypothesis then we have got to show that there is something wrong with the simple idea that we could measure anything we please as accurately as we please. We shall discuss the case of the electron because on account of its being the lightest thing in the world, it provides the most crucial case ; the uncertainties for other bodies are always less, and are small beyond conceivable observation for bodies of ordinary size. We have got to show that it is not possible to measure simultaneously the position and speed of an electron with precisions higher than those allowed by the Uncertainty Principle ; and we must recognise that if any one can contrive a method by which he can better these precisions, then the whole structure of

modern physical theory collapses, and we know nothing about the foundations of nature. It was the great achievement of Heisenberg to show that all is well with our theories.

We have to devise an experiment which is simultaneously to fix the position and velocity of an electron with the highest possible precision. The easiest way to fix a position with accuracy is to take a microscope, and we can simplify the question of speed by supposing the electron motionless. Our experiment then consists in looking through a microscope at a stationary electron ; it is not actually a practical experiment, though very nearly so, but that does not matter because our object is to prove that it would not work with unlimited accuracy even if it were practical. We now have to consider the question of the accuracy of our instrument. The question of speed is easy, because, if the electron stays near the same place for a considerable time, it obviously has very small speed, and so we can check the speed to be zero as closely as we like by taking a long time over the observations. As to the accuracy with which we can observe the position, I must cite certain well-known characteristics of the microscope. If we take the highest possible power of a microscope, and look at a series of objects each smaller than the last, we find that though the larger ones can be seen in sharp detail, when we come to the smaller ones that is not so-- their sharper corners seem to be rounded and hazy ; and finally we get down to objects which can only be seen as round discs, though they may really be as angular as the larger ones. This failure is easily explained from the wave theory of light ; it is never possible to

see detail of a scale smaller than the wave-length of the light illuminating the object. The wave-length of visible light is about one-twenty-thousandth of a centimetre, and so if we are to use ordinary light we certainly cannot decide the position of our electron more precisely than this. We can do better, however, by imitating the process used in microphotography, which considerably extends the range of visibility by the use of ultra-violet light. But whereas in the practical technique of the microscope it is hardly possible to double the resolution by these means, we are not so limited in our idealised experiment ; we may take a wave-length many thousand times smaller. For our purpose the X-rays would be good, but still better are the  $\gamma$ -rays of radium, which have a wave-length about a hundred-thousandth of that of visible light, say, roughly, a ten-thousand millionth of a centimetre. With a microscope using this illumination we really can do something. But when we set the apparatus up we find a curious thing ; the electron may be there at the beginning of the experiment, and may be at rest, but something always happens so that the electron gets knocked away, and our experiment is ruined every time. We must see how this comes about.

About nine years ago, A. H. Compton was led to consider the question of the way in which an electron would react to light. This is, of course, an old problem, but the virtue of Compton's method was that he regarded it as a collision of two bodies, a light particle and an electron-particle. This was long before the wave aspect of the electron was dreamt of, and though the particle aspect of light was known, no one had as

yet taken it so seriously. He found that an electron can only scatter light by itself being set in motion, and worked out the various relations for the scattering of the light and the recoil of the electron. He then verified his predictions very fully, so that in speaking of the Compton effect we are not referring to an abstract doctrine but to hard fact. Compton showed that the recoil of the electron is insignificant for visible light, is easily perceptible for the shorter wave-length of X-rays, and attains very large values if the light has the extremely short wave-length of the  $\gamma$ -rays.

We can now see where our experiment is going to go wrong. We may compare our problem to that of the biologist who wants to study the life-history of some cave-dwelling animal which dies if the faintest light falls on it; the animal is killed by the mere attempt to see how it lives. In our case there is no difficulty about imagining that an electron-particle is absolutely at rest in some absolutely exact place, but it is useless to imagine it because it is unverifiable. We cannot verify that it is there without light to see it by, and if we want to know the position with high accuracy we must use  $\gamma$ -ray light. But this light can only reveal the electron provided it is scattered by the electron; and when it is so scattered there is bound to be a recoil, so that even if the electron was at rest before, it will not be at rest after the scattering. So we cannot fix the position exactly without thereby spoiling the velocity. If, on the other hand, we are content with a rather rough knowledge of the position we might use ordinary light in our microscope, and thus only get a very small recoil; we have

sacrificed knowledge of position and have gained a greater precision in our knowledge of the speed. When it is worked out in detail, the result of our experiment is in exact conformity with the Uncertainty Principle; that is to say, we can fix either position or speed as accurately as we please, but either only at the expense of the other.

The microscope is evidently not going to help us in breaking the Uncertainty Principle, because of the tiresome way in which the light makes the electron recoil, and we therefore try again, this time without the use of light. Suppose, for example, that we have a source of electrons to the left of two screens. The screens have very fine holes cut in them, which are closed with shutters most of the time. We first open the left-hand shutter for an instant, and then the right-hand one for an instant. Any electron which is found to the right of both screens must have come along the line of the holes, and must have taken a definite time in doing so. Surely we now know position and velocity as accurately as we like, by making the holes very small and only opening them for very short times. Quite true; we can say where the electron was, but not where it is, since on its emergence from the second hole the electron will be scattered into some arbitrary direction, like the wave going through the gap in the sea-wall. We have, in fact, only succeeded in practising the noble art of foretelling the past. Once again we see that our idea of the particle as occupying a sequence of exact positions is a useless one, because the experiment devised to tell us what the position is will always disturb the particle, giving it a velocity that it would not have had if we had

not made the experiment, and so making the determination useless.

The general outcome of this and other experiments is always the same, and may be summarised thus. If we were conservative and did not believe in all the new ideas, we should regard the electron as a little piece of grit, and therefore located at some precise place and possessing some definite speed of motion all the time. But in adopting this belief we lay ourselves open to the challenge of being asked to prove what the position and velocity are ; and when we come to examine the details of the appropriate experiments, we find that the values will always elude us, and remain undecided to just the extent suggested by the Uncertainty Principle. There is, therefore, no warrant for our conservative assumption, and, on the other hand, there is no contradiction in the dualistic ideas of wave and particle. Before going on I ought to say that I have simplified the question by only discussing the case of the electron. The Uncertainty Principle applies to everything else as well, and the only reason why I have not discussed the other cases is that the electron provides the extreme case, so that if it can be met there, all the others are easy.

The Uncertainty Principle has very radically altered our views about one of the fundamental principles of knowledge, the principle of causality. We used to think that there was an absolute causality in the world ; that a full knowledge of the present would inevitably lead to certainty about the future. It is true that the force of the principle was much reduced by the fact that we usually had to confess to so much ignorance about the

present that we could excuse ourselves from any great self-confidence in prophecy ; but we used to feel it as a slight reproach that we suffered from this ignorance, and to imagine that our descendants would become perfect prophets because they would be omniscient. But now we see that the present is definitely unknowable, so that there is no possibility of foretelling the future with certainty. Every time we determine something in the present we spoil something else ; and we are always at least one step behind what we need for the purpose of confident prophecy. Instead of certainties we have to deal with probabilities, and the theory of chance is raised to a more dignified position than it used to occupy ; it is no longer a confession of ignorance of things we feel we ought to know, but of things essentially unknowable.

Closely allied with the question of causality is the question of free will and determinism, which has puzzled the philosophers of all ages. It is really not a matter for the scientist, but it is impossible to conclude without a reference to it. What I am now saying has none of the authority of scientific knowledge behind it, and it is improbable that any one will agree with it. I can lay no claim to philosophic knowledge, but my views certainly resemble those held by some philosophers in this, that they change every few months. In spite of the great effect that the new theory has on the idea of causality I believe it leaves the question of free will where it was.

There appear to me to be two radically different kinds of free will, which may be called *my* free will and *your* free will. When I think

about my free will, I conceive myself standing right outside the operations of nature, making arbitrary decisions without reference to causes of any kind, such as the decision whether I shall raise or lower my hand. When I observe your free will, it seems to me to be a very inferior thing, a certain capriciousness in your actions, for example a perfect uncertainty as to whether you will raise or lower your hand ; in fact, though you claim that you are really displaying my kind of free will, yet as far as my observation goes your actions have the same sort of uncertainty as that displayed by an electron. It used to be felt by some that the old inexorable laws of nature allowed no latitude for this capriciousness, and that now that we have found that those laws were wrong, we have escaped from the rigid determinism that they implied. I do not think this is the real point. Though the behaviour of a single electron is very uncertain, that of a thousand will be fairly regular, and when we come to the large number of electrons in the human body we expect a very complete regularity. The human body will be governed by the new laws of nature almost as rigorously as by the old but when we consider the enormous complication of a human being, and the complete impossibility of knowing even roughly what all the parts of the human machine are doing, this rigour need not trouble us, for even before the advent of the Uncertainty Principle our ignorance was surely ample enough, and was evidently always going to be ample enough, to prevent any confident forecast of our actions. So I conclude that there was no great difficulty about *your* free will even before the discovery of the new principles, and that the philosophic



difficulty is just what it was before, the intolerable contradiction between *my* free will and *yours*.

It is possible that these difficulties will always remain to puzzle us, but it really does not seem to matter very much whether they do, whatever their appeal to the introspectionist may be. It is the scientific meaning of the new theory that is of permanent value. The earlier direct experiments with atoms revealed certain contradictions. The new quantum theory removed these contradictions, but seemed at first to be composed of the most fantastic abstractions. It was the Uncertainty Principle that revealed the common sense of these abstractions.

[C. G. D.]

Friday, March 4, 1932

SIR ROBERT ROBERTSON, K.B.E., M.A.,  
F.R.S.,  
*Treasurer and Vice-President, in the Chair*

BRIG.-GENERAL SIR HAROLD HARTLEY,  
C.B.E., M.C., M.A., F.R.S.,  
*Director of Scientific Research, London, Midland  
and Scottish Railway Company ; Research  
Fellow of Balliol College, Oxford*

## MICHAEL FARADAY AND ELECTRO- CHEMISTRY

THERE is no need to remind you of the close association of the Royal Institution with the early history of electro-chemistry, for it must be amongst your proudest memories. In this building Davy carried out his investigations of the chemical effects produced by an electric current, which culminated in the isolation of the metals sodium and potassium in 1807, one of the most dramatic discoveries in the history of Chemistry. Twenty-five years later it was here, too, that Faraday established the fundamental laws of electrolysis by the researches which are the subject of my discourse this evening.

I am not going to speak to you so much of the results of Faraday's discoveries, but rather to trace the way in which those discoveries were

made, with the aid of the pages of his diary. Faraday's diary is a unique scientific and human document, in which he recorded in numbered paragraphs, which ran to 16,041, not only the results of his experiments, but the ideas that flashed on him as he was working in the laboratory, and his plans for new researches. By means of it we can follow his progress from day to day, and watch the interplay of ideas and experiments, and the swiftness and certainty with which he reached a decision.

When Faraday was still a bookbinder's apprentice, his eager curiosity was excited by the discoveries of Davy, and he made experiments on the electrolysis of solutions with home-made batteries, consisting of discs of zinc and half-pennies, when half-pennies cannot have been too plentiful with him. In 1813, at the age of twenty-two, he came to the Royal Institution to be Davy's assistant. You know the romantic story how Faraday was brought to hear Davy's last lectures in this theatre, and made detailed notes which he bound and sent to Davy for correction, and how Davy was so much impressed by them that he invited Faraday to be his assistant when a fortunate vacancy occurred. I often marvel at that slender chain of events which was destined to mean so much to the progress of science.

Faraday served his apprenticeship to Chemistry under Davy in this building. He soon began to carry out investigations himself, and from 1816 onwards a constant stream of papers appeared under his name. They form no connected series, and there was no general idea underlying them, but they ranged over the whole field of chemistry

—physical, inorganic, and organic. The papers reveal Faraday's skill as a practical chemist, the neatness and simplicity of his experimental methods, and the quickness and accuracy of his observations. They are mainly records of experiments, as, owing to Faraday's scepticism regarding the atomic theory, probably acquired from Davy and Wollaston, he seems to have taken little interest in the problem of the atomic constitution of substances which was just beginning to perplex chemists. When he discovered naphthalene-sulphonic acid, he called it "sulphonaphthalic acid, which," he said, "sufficiently indicates its source and nature without the inconvenience of involving theoretical views." But in those years Faraday was gaining the first-hand acquaintance with the properties of many substances, which was to prove invaluable to him in choosing the right materials for his experiments. He was also accumulating an unrivalled knowledge of chemical technique, and gaining the confidence and certainty to which ~~was~~ due the boldness and directness of his experiments in the years to come. In 1827 he published his book on "Chemical Manipulation," in which he describes every kind of laboratory operation and device. It is one of the most personal documents in scientific literature, as every page is a record of his own experimental methods, and it reveals how every detail of each operation had been studied by him and reduced to its simplest and most effective form.

The year 1831 was the turning-point in Faraday's career. There is no greater contrast in scientific literature than his earlier chemical papers characterised by their essentially practical

outlook and accomplishment, and the brilliant flights of imagination that inspired his "Experimental Researches in Electricity."

Many reasons have been given to account for this sudden transformation—that Faraday's powers were maturing gradually in readiness for that great outburst of intellectual activity in his fortieth year—that he had fallen in love; but we know that Faraday fell in love in 1820, and remained in love all his life: besides, I have never observed that that particular form of pre-occupation has been prolific in scientific discoveries—that Faraday had been elected to the Royal Society: but that happened in 1824—that he had been released from the tutelage of Davy: but he was made Director of the Royal Institution laboratory in 1825, when he instituted these Friday evening discourses.

No. I am convinced that it was the discovery of electromagnetic induction, the success of an experiment which Faraday had previously tried again and again without result, that gave the new impulse to his work and gave him confidence in the promptings of his imagination. What are the facts?

Electricity was one of Faraday's earliest scientific interests. Long before he went to Davy he was experimenting with home-made batteries. Already in 1816 we get a glimpse of his intuitive belief in the essential unity of the forces of nature, which was to influence so greatly the current of his researches. His first lecture to the City Philosophical Society was on the general properties of matter, and we find him speculating on the forces underlying material behaviour and on their inter-relation. "That

the attraction of aggregation and chemical affinity is actually the same as the attraction of gravitation and electrical attraction I will not positively affirm, but I believe they are " In 1821, Faraday repeated the experiments of Oersted, Arago, and Ampère on electro-magnetism and discovered the rotation of a wire carrying a current if free to move round a magnetic pole. Magnetism had been produced from electricity, and Faraday was convinced of the possibility of obtaining electricity from magnetism. In 1824 he was experimenting with a magnet in a helix connected with a galvanometer, without result, and similar experiments were made in 1825 and 1828. Either the galvanometer was too insensitive or he failed to notice the momentary deflection when the magnet was introduced. On August 29th, 1831, the induced current was detected—Faraday's dream had come true—and ten days of decisive experiment ended in his paper on "The Induction of Electric Currents," which was to shape the future of electrical science and electrical industry. ~

It is significant of Faraday's train of thought that the first experiment he made on August 29th, 1831, after discovering the induced current, was to attach platinum wires to the ends of the coil and see if he could detect any decomposition in a drop of copper sulphate solution. The test was not delicate enough, and he did not succeed in detecting the chemical power of magneto-electricity until several years later. However, he made a number of experiments on chemical means of detecting the current from a voltaic cell, and on June 11th, 1832, he found in bibulous paper moistened with potassium iodide and starch the most sensitive detector.

His discovery of electro-magnetic induction raised afresh in Faraday's mind the old and still disputed problem of the identity of electricities from different sources, and chemical action was one of the tests he applied to its solution. Having shown that common (frictional) voltaic and magneto-electricity all produce similar physiological, magnetic, chemical, and thermal effects, Faraday sought to establish their identity by quantitative experiments. Among the discoveries that Cavendish had made almost fifty years previously, was that the behaviour of an electric charge depends on two factors, the degree of electrification (or potential as we should call it) and the size of the charge. His paper on the torpedo, published in 1776, contains an account of experiments with Leyden jars which demonstrate very clearly this distinction. Faraday had read Cavendish's paper and realised that his theory explained the apparent differences in behaviour of frictional and voltaic electricity. He says: "The beautiful explication of these variations afforded by Cavendish's theory of quantity and intensity requires no support at present, as it is not supposed to be doubted." \* The theory was, however, by no means generally accepted in 1832, but Faraday's recognition of its truth was the key to the success of his researches on electro-chemistry.

He started out to prove that the effect on a galvanometer of a discharge of frictional electricity was dependent on its quantity and not on its intensity, which he showed on September 14th, 1832, by charging 8 Leyden jars in a battery of 15 by means of 30 turns of a frictional machine,

\* "Experimental Researches," Vol. I, p. 81 (1833).

and seeing that when discharged through the galvanometer they caused the same throw of the needle as the whole 15 jars charged by means of 30 turns, although an electrometer indicated that the intensity of the charge was roughly one-half in the second case. "Hence," said Faraday, "it would seem that if the same absolute quantity of electricity passed through the instrument whatever may be its intensity, the deflecting force is the same."

He then made a small "standard elementary battery," consisting of platinum and zinc wires  $\frac{1}{16}$ th inch in diameter, and  $\frac{1}{16}$ th of an inch apart, which he immersed to a depth of  $\frac{3}{4}$ th inches in dilute sulphuric acid (one drop of acid in 4 oz. water), and he found that by immersing the wires for 8 beats of his watch (3.2 secs.) when they were joined to a galvanometer, the momentary deflection of the needle (its half period of swing was 6.8 secs.) was the same as that caused by 30 turns of the machine. Hence, said Faraday, the amount of electricity produced by the cell in this time was the same as that produced by 30 turns of the machine. He next compared the amounts of chemical change by allowing the electricity to pass in both cases through filter paper moistened with potassium iodide on a platinum spatula with a platinum wire  $\frac{1}{16}$ th inch in diameter as the positive pole. A brown circle of iodine was found at the point of contact and its tint depended on the number of turns of the machine. Faraday showed by varying the number of turns of the machine that it required approximately 30 turns to produce an iodine spot of the same tint as that given by immersing his standard battery for 8 beats of his watch. "Hence it would appear



that both in magnetic deflection and in chemical effect the current of the standard voltaic battery for 8 beats of the watch was equal to the electricity of 30 turns of the machine, and that therefore common and voltaic electricity are alike in all respects."

I have described the experiments made on September 14th and 15th, 1832, in detail, as they were the first attempt to connect the quantity of electricity passing in an electric current with the amount of chemical decomposition accompanying it, and there is no better example of the neatness, the simplicity, the directness, and the conclusiveness of Faraday's experimental methods. When everything was ready for the attack, two days sufficed to reveal to Faraday the fundamental relation which was to shape the course of his future work. The paper on "The Identities of Electricities" was not published until December 10th, an unusually long delay for Faraday; but in the interval he did no more experiments, and the paper contained the first statement of his First Law of Electrolysis: "It also follows that for this case of electro-chemical decomposition, and it is proved for all cases, that the *chemical power, like the magnetic force, is in direct proportion to the absolute quantity of electricity which passes.*"

Faraday's actual researches on electro-chemistry occupied the next eighteen months of his life. The three main problems with which they deal are :—

1. The mechanism of conduction in solution and the dependence of the passage of the current on chemical decomposition.
2. The amount of chemical action accompanying the passage of the current.

3. The source and the intensity of the current produced by voltaic cells.

Owing to Faraday's association with Davy the problem of conduction in solutions was not new to him, and a sentence in his letter to Richard Phillips on November 29th, 1831, describing his discovery of electro-magnetic induction, shows his interest in it: "I believe it will explain perfectly the transference of elements between the poles of the pile in decomposition."

The main experimental facts had been known to Faraday since the days when he experimented with a home-made battery while he was still a bookbinder's apprentice. Pure water would not conduct a current, but the addition of acids or salts made it a good conductor, and at the same time decomposition occurred, the products being liberated not in the body of the solution, but at the surface of the metallic conductors, which were called the poles. The word "pole," from its association with the magnet, suggested the idea that the decomposition was due to attraction or repulsion caused by the poles. With most acids and bases, and also with a number of salts, the products were hydrogen at one pole and oxygen at the other. In the presence of certain salts, such as copper sulphate and lead acetate, the metal was deposited at the negative pole instead of hydrogen. In the case of salts such as sodium sulphate, acid was liberated at the positive pole and alkali at the negative.

In trying to find the most delicate test for the passage of electricity, Faraday made many new experiments on the chemical action produced by a current. In one of them he placed one end of

a long piece of litmus paper moistened with sodium sulphate in contact with an electrical machine, while the other end was held opposite to the discharging points. On turning the machine Faraday saw that decomposition took place, the paper becoming red "where the positive electricity entered from the air." This proved to him that the decomposition was not dependent on the presence of metallic poles in the solution, and on September 6th he wrote in his note-book: "Hence it would seem that it is not a mere repulsion of the alkali and attraction of the acid by the positive pole, etc., etc., but that as the current of electricity passes whether by metallic poles or not the elementary particles arrange themselves and that the alkali goes as far as it can with the current in one direction and the acid in the other. The metallic poles used appear to be mere terminations of the decomposable substance.

"The effects of decomposition would seem rather to depend upon a relief of the chemical affinity in one direction and an exaltation of it on the other rather than to direct attraction and repulsions of the poles." Here we see the germ of Faraday's ideas on the nature of electrolysis.

In October and November 1833, only two days were spent on electrical experiments, but Faraday was constantly thinking of the mechanism of conduction in a solution, and suddenly on December 24th he wrote: "Can an electric current, voltaic or not, decompose a solid body, ice, etc., etc.? If it can does it give structure at the time? If it cannot what would fused gum, lac, wax, etc.?" A cold spell at the end of January enabled him to put this to the test, and he found

that while ice would not conduct a voltaic current conduction occurred immediately the ice melted. "If ice will not conduct is it because it cannot decompose?"

It was characteristic of Faraday's thoroughness that he went on to examine the conductivity in the fused state of a number of substances which are solid at ordinary temperatures, and to study the products formed during electrolysis. It was a new field for him and he showed his usual experimental skill in devising simple methods for working at high temperatures, including even the use of the oxyhydrogen blowpipe. During February and April he examined over 130 substances and found that while a number resembled water in being insulators in the solid state and becoming good conductors if fused, when they were decomposed by the current, certain of them, such as boric acid, did not conduct when fused. He thus arrived at no general conclusion, but the experience he gained in working with fused salts was to prove invaluable later in the year in his work on electro-chemical equivalents. The experiments were finished on April 22nd, and on April 24th they were communicated to the Royal Society with the title, "On a New Law of Electric Conduction."

Faraday then turned his attention to the mechanism of conduction in a solution. On May 2nd he passes a strong current through a saturated solution of sodium sulphate and examines it with polarized light both across and along the direction of the current to see if he can detect signs of arrangement of the molecules, but without result. On May 20th he determines the transfer of sulphuric acid during electrolysis by

measuring the changes in concentration in two vessels connected by moist asbestos, and on May 27th he shows that the transfer of sulphuric acid differs from that of sodium sulphate of equivalent concentration, "very evident therefore that the transfer is dependant on the mutual action of the particles." He summed up his views in a paper to the Royal Society on June 18th, the main conclusion being "that electro-chemical decomposition does not depend on the simultaneous action of two metallic poles," and the effects of it "are due to a modification, by the electric current, of the chemical affinity of the particles through or by which that current is passing, giving them the power of acting more forcibly in one direction than in another, and consequently making them travel by a series of successive decompositions and recompositions in opposite directions, and finally causing their expulsion or exclusion at the boundaries of the body under decomposition."

In May 1833 Faraday's thoughts were returning to the question of the amount of chemical action that takes place during the passage of a current. On May 16th no experiments were recorded in the note-book, but among the ideas he jotted down was: "Is the law this (above a certain intensity, *i.e.* the one required for decomposition to take place at all), that whatever the size of plates, or number intervening, or constant section of decomposing matter, or variable section, or variable strength, or number of series in the battery: that . . . equal currents of electricity measured by the galvanometer evolve equal volumes of gas or effect equal chemical action in a constant medium?" A week later he writes

down his plans for testing the law : “ By putting cups and expts. in succession and sending the same electrical current through both or all am sure that each is submitted to an equal force. Can try well this way whether the same quantity of different intensity does the same chemical work using same dilute sulphuric acid but different-sized poles, and collecting gas, and that will tell —some poles mere wires, others large plates.” Three months elapsed before he actually carried out the experiment. On August 27th he wrote : “ Pursue the investigation, whether the same quantity of electricity always produces an equivalent of chemical decomposition. . . .” On August 30th he found, as he expected, that the same amount of current liberated the same volume of gas irrespective of the concentration of the acid, the size of the electrodes, or the intensity of the current. He obtained the same results with solutions of various salts, and his comment was : “ Strange that with such different substances the same quantity of water should be decomposed by the same current.” These experiments were continued in September, and Faraday was constantly puzzling over the effect of various substances in increasing the conducting power of water. On September 17th he showed that cells containing muriatic and sulphuric acids had given the same volume of hydrogen when connected in series, and he was now busy constructing a simple apparatus to measure the quantity of electricity by means of the volume of gas produced by it. “ The instrument offers the only *actual measurer* of voltaic electricity which we at present possess . . . I have therefore

named it a volta-electrometer." \* To-day, following Faraday, we define our practical unit of current by its electrolytic action, and we use his name to denote the fundamental unit of electro-chemistry.

On September 19th, among his observations, he notes: "Will not white-hot diamond conduct? If so may perhaps crystallise carbon at white heat by power of the voltaic battery."

He had been worried by the contraction, on standing, of the mixture of oxygen and hydrogen obtained in the electrolysis of sulphuric acid. He traced this to the catalytic activity of the platinum electrode, and showed that the positive and not the negative was effective. This observation led him to spend some weeks investigating the conditions under which platinum and other metals would assist the combination of various gases, when he discovered the retarding effects caused by small quantities of gases such as olefiant gas, carbonic oxide, and sulphuretted hydrogen. The results were communicated to the Royal Society on November 30th.

Faraday then returned to the investigation of the amount of chemical action produced by the current, and as he recognised that in the electrolysis of aqueous solutions it was doubtful whether the elements liberated at the poles were to be regarded as primary or secondary products, he extended the inquiry to include fused substances, which would be free from this ambiguity.

Hitherto Faraday had only compared the quantities of the same substance, such as hydrogen liberated by the same current in a series of cells, but he now began to consider the relative quanti-

\* The name was contracted to voltameter five years later.

ties of different elements that would be liberated by the same current. On September 23rd he wrote: "Think it will be very important to have a new relation of bodies, under the term electro-chemical equivalents, tabulated. Very important as to decomposing powers of the pile, as to the true expression of equivalent numbers, and as to nature of chemical affinity and its relation to electrical states and powers."

On September 28th in discussing the results of experiments in which a current is passed through a sulphuric acid voltameter, and various solutions in series with it, Faraday decided that in aqueous solution the current is probably carried by hydrogen and oxygen, these being always the primary products of electrolysis. "When, therefore, metallic solutions are decomposed the metals are evolved not by the current of electricity but by the hydrogen evolved at the N. Pole. . . . Hence it will probably follow that in these cases the metal is an equivalent of the hydrogen because it is produced chemically by the hydrogen, and therefore such effects will not prove the equivalent character of the products of true electro-chemical decomposition . . . Perhaps fused nitre will be a good salt to compare by current with decomposition of water. Or fused chloride of lead or tin." These experiments with fused salts, which removed any doubt as to whether the elements liberated during electrolysis were primary or secondary products, were not carried out until December, but doubtless in the interval Faraday was making plans for them.

On December 17th he wrote in his note-book: "Proceeded to decompose dry chlorides, oxides, etc., to ascertain if there also the decomposition



was definite and what the equivalent numbers would be." So quickly was the final stage in the investigation accomplished that on January 9th, 1834, the paper containing the Laws of Electrolysis was communicated to the Royal Society. In the first experiment on December 17th fused stannous chloride in a glass tube was decomposed with platinum wire poles with a voltameter in series, and the weight of the tin liberated compared with the weight of water (0.26486 grain) decomposed in the voltameter. "1.76 of tin had been electro-chemically evolved at the exode, and of course a corresponding portion of chlorine at the cisode.

W            T

Now  $0.26486 : 1.76 :: 9 : 59.805$  the tin.

The number for tin is given 58 which is very near indeed for a first experiment, and shows that the electro-chemical equivalent is the same as the chemical equivalent here." Note Faraday's first efforts at a new terminology, "exode" and "cisode." Later on the same day the word "pole," which suggests the idea of attraction or repulsion, was struck out and "electrode" written above it for the first time.

On the following day another experiment with stannous chloride gave a value of 53.833 for tin. Two similar experiments with fused lead chloride gave electro-chemical equivalents for lead of 105.11 and 97.22, the chemical equivalent being 103.5 or 104.

Faraday wrote of the lower value: "Hence it is too little, but still so near as to establish the principle of electrochem equivalents."

On December 19th no experiments are

recorded, but doubtless Sergt. Anderson was helping Faraday to set up apparatus, and fresh glass vessels with fused-in electrodes had to be blown for each experiment. A few extracts from the note-book on that day show the activity and range of Faraday's mind :—

1192. "With regard to intensity and its meaning, etc. Define intensity if possible and state its relation to quantity, time and conducting power."
- 1195-1200. "Nervous agency of Electricity."
1207. "In the table I mean Real Electro chemical equivalents not hypothetical for we shall else outrun fact and lose the information directly before us. . . . I must keep my researches really Experimental and not let them deserve anywhere the character of hypothetical imaginations."
1212. "Search for Fluorine by using a plumbago Pos. Pole acting on a fluoride."
1213. "This process may finally give rise to some very good processes of analysis in determining weights or at least to some excellent modes of comparing weights of metals . . . a good principle of analysis for it will hold probably in salts as well if properly selected and may use mercury electrodes when convenient."

A remarkable anticipation of modern methods of electrolytic analysis.

With the exception of Christmas Day, determinations were made every day. On December 26th Faraday comments in his diary on the enormous quantity of electricity required to decompose a small amount of water. Later he estimates that 800,000 charges of a Leyden battery, each one of which would suffice to kill a cat, "would be necessary to supply electricity sufficient to decompose a single grain of water ; or, if I am right, to equal the quantity of electricity which is naturally associated with that

grain of water, endowing them with their mutual chemical affinity!"

The experiments on the electrolysis of fused salts were difficult and often gave inconclusive results, but confirmatory evidence was obtained from lead borate and iodide.

Faraday was anxious to extend the work to the deposition of metals from aqueous solutions, and he found that zinc deposited on a platinum electrode gave an electro-chemical equivalent of 34.08, while the loss in weight of amalgamated zinc in contact with platinum compared with the weight of hydrogen evolved gave in two experiments equivalents of 30.2 and 32.31. "Excellent," he writes after the latter result, to which he attached great importance, as it was the first occasion on which he had compared the amount of chemical action in a voltaic cell with that produced by the current in the external circuit. This confirmed his conviction "that the quantity of electricity which, being naturally associated with the particles of matter, gives them their combining power, is able, when thrown into a current, to separate those particles from their state of combination; or, in other words, that the electricity which decomposes, and that which is evolved by the decomposition of a certain amount of matter, are alike.

"The harmony which this theory of the definite evolution and the equivalent definite action of electricity introduces into the associated theories of definite proportions and electro-chemical affinity is very great. According to it, the equivalent weights of bodies are simply those quantities of them which contain equal quantities of electricity . . . it being the ELECTRICITY which

determines the equivalent number, because it determines the combining force. Or if we adopt the atomic theory or phraseology then the atoms of bodies . . . have equal quantities of electricity naturally associated with them. But I must confess I am jealous of the term atom, for though it is very easy to talk of atoms, it is very difficult to form a clear idea of their nature."

These sentences must have been written immediately after the experiments were made, as the paper was communicated to the Royal Society on the same day (January 9th). During these three weeks Faraday worked at very high pressure, and it was no wonder that on January 7th he wrote: "I wish I could evolve time from the battery as well as all these points and then. . . ." He was true to his maxim: "Work. Finish. Publish."

The paper itself is the most important of Faraday's contributions to electro-chemistry, and in it he summarises all his previous work. He begins by introducing the new terminology which he devised with the help of Whewell for the sake of greater precision of expression, and all his new names—electrode, anode, cathode, ion, anion, and cation, electrolyte and electrolysis – we use to-day with the significance which Faraday gave to them. After a short account of the conditions necessary for electro-chemical decomposition, he describes his new volta-electrometer and the evidence that led him to the conclusion that the amount of chemical action is dependent solely on the amount of electricity that passes through it. He next discusses whether the products of electrolysis are primary or secondary, and gives his evidence for

the identity of chemical and electro-chemical equivalents.

The researches had strengthened enormously the evidence for his First Law of Electrolysis—"The Chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes"; and they had established the Second Law- "Electro-chemical equivalents coincide, and are the same with ordinary chemical equivalents."

The exactness of these two laws has been confirmed by every subsequent investigation.

For three weeks he tried to isolate fluorine, and on February 10th thought he had obtained it by the electrolysis of fused lead fluoride. "Must now lay this subject aside for a while and go to the trough." Faraday spent a month carrying out a large number of experiments on the intensity required to produce electrolysis of different solutions by varying the number of cells in the battery and seeing how many were required to electrolyse various compounds in solution or in a fused state. One of his difficulties was that he had no unit to measure by, and on February 10th he notes, "The power of decomposing water a good unit of intensity in voltaic apparatus."

The general result of these experiments was to strengthen Faraday's conviction that the source of the current was the chemical reaction taking place in the voltaic cell and not the mere contact of two metals, and indeed he proved that a current is produced without such contact by interposing a slip of paper moistened with potassium iodide solution between the metals. His thoughts were concentrated on the relation between chemical action and the production of electricity, and he

realised that whether a current passes or not depends on the relative magnitudes of the chemical affinities of the reactions taking place in the battery and in the electrolytic cells. In discussing this problem on February 12th he writes : " The whole arrangement seems beautifully to show that antagonism of the chemical powers and the Electromotive parts with the chemical powers and the interposed parts. The first are producing electric effects, the second opposing electric effects, and the two seem equipoised as in a balance, and in both cause and effect appear to be identical with each other. Hence chemical action merely electrical action and electric action merely chemical." Again on February 19th : " Affinity is action at both points, but is as it were connected or related by the current of electricity in the communicating wires, or in other words affinity is electricity and vice versa."

Three days later he wrote : " We seem to have the power of deciding in certain cases of chemical affinity (as of zinc with the oxygen of water) which of two modes of action of the one power shall be exerted. In the one mode we can transfer the power on it being able to produce elsewhere its equivalent of action, in the other it is not transferred on but exerted at the spot. The first is the case of voltaic electric production, the other the ordinary cases of chemical affinity. But both are chemical actions and due to one power or principle."

In other words Faraday saw that a chemical reaction can be carried out in two ways, either by means of a voltaic cell in which the reactants are separated by an electrolyte, or by their direct contact, and further, he identified the electro-

motive force of the cell with the chemical affinity of the reaction. Half a century was to elapse before the conception of chemical affinity assumed a definite form in chemists' minds, but here Faraday anticipates our modern interpretation. His method of reasoning, too, is an instinctive recognition of the Law of Conservation of Energy, and it was in connection with the chemical theory of the cell that he wrote in 1840: "In no case . . . is there a pure creation or production of power without a corresponding exhaustion of something to supply it."

All these results were collected in a paper, "On the Electricity of the Voltaic Pile," and communicated to the Royal Society on April 7th. This was really the last of Faraday's great contributions to electro-chemistry, although a few papers of minor importance came later. The intensity of the current was a much more complex problem than electro-chemical equivalents, and Faraday only succeeded in associating it with the chemical affinity of the reaction in the cell. A quantitative solution of the relationships between electromotive force, the resistance of the circuit and of the electrolyte, and current strength was only possible in the light of Ohm's Law. This had been published in 1827, but Faraday could not read German, and apparently did not know of it during the period of his electro-chemical researches; so that elucidation of the quantitative relationships between the factors he was considering was left to a later generation of physicists.

Faraday's researches had a most profound and immediate effect on the progress of electro-chemistry. Within two years he changed the whole aspect of the subject and gave it a coherent

structure and a quantitative basis, as a result of his laws of electrolysis, his new ideas which were crystallised in his new nomenclature, and his association of the intensity of the voltaic cell with the chemical affinity of the reaction taking place in it. To-day his ideas seem to us so clear and obvious that it is hard to appreciate their significance to his contemporaries. Faraday's success was due primarily to the instinct which guided him unerringly through the maze of experimental facts which might so often have led him astray, and kept as his objective the fundamental factors in each problem. Undoubtedly he was helped enormously by his wide knowledge of chemistry and the properties of chemical substances. He was never deterred by experimental difficulties, and there was a masterly touch in the simple and direct solutions he found of them. Faraday's electro-chemical researches rank among the highest of his achievements. They were carried out in a short space of time with amazing economy of effort, thanks to the combination in him of brilliant imagination, unerring instinct for essentials, and unrivalled mastery of experimental technique.

It is remarkable how many of Faraday's ideas and discoveries had a decisive influence on the development of electro-chemistry in the nineteenth century, and have even to-day a direct bearing on modern theories. His experiment on the transfer of sulphuric acid during electrolysis inspired the investigation of Daniell, which proved that the current in aqueous solution is carried by the ions of the solute, and not as Faraday supposed by the ions of hydrogen and oxygen. Later its development of Hittorf led to the conception of



transport numbers, which has played so important a part in the theory of solutions.

Again, in 1834, Faraday pointed out that if "we adopt the atomic theory or phraseology then the atoms of bodies . . . have equal quantities of electricity associated with them." Had he been a believer in the atomic theory he might have made the deduction that electricity, like matter, is atomic in nature. It was left most appropriately to Helmholtz in his Faraday lecture given in this theatre in 1881, to point out this most startling result of Faraday's laws: "If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into elementary portions, which behave like atoms of electricity." Thus Faraday's laws lead directly to the conception of the electron.

One further example. Faraday first pointed out the enormous size of the electrical charge carried by each ion. Chemists and physicists lost sight of this fact until Helmholtz recalled their attention to it fifty years later in his Faraday lecture, and showed that the attractive force between the electrical charges associated with hydrogen and oxygen is 71,000 billion times greater than the gravitational attraction between their masses. The next twenty years saw the rise of the ionic theory of Arrhenius and Ostwald, and its many triumphs in the field of weak electrolytes, but it always failed to account for the behaviour of strong electrolytes. These were said to be anomalous because they did not conform to a theory which neglected entirely these vast interionic forces. It was not until 1912 that Milner proved that as a result of interionic forces

the ions are not distributed at random in a solution, and that there must be an excess of positive ions in the neighbourhood of each negative ion and vice versa. Each ion must therefore be regarded as surrounded by an ionic atmosphere of the opposite kind, and Milner was able to show that the effect of the atmosphere on the central ion accounted for certain of the properties of strong electrolytes. In 1923 Debye and Hückel found a general mathematical solution of the problem of interionic forces in dilute solutions, and succeeded in calculating the effect of dilution on both the activity and mobility of any ion, on the assumption of complete dissociation. There is thus a direct line between the observation made by Faraday and the most modern theory of solutions.

This illustrates once again the marvellous intuition which guided Faraday to the fundamental aspects of any problem. As Kohlrausch said of him: "Er riecht die Wahrheit"—he smells the truth; or in Tyndall's words, "Faraday was more than a philosopher: he was a prophet."

[H. H.]

Friday, March 18, 1932

MAJOR CHARLES E. S. PHILLIPS, O.B.E., F.R.S.E.  
*Secretary and Vice-President, in the Chair*

LORD RUTHERFORD OF NELSON, O.M., M.A.,  
D.Sc., LL.D., F.R.S., M.R.I.  
*Cavendish Professor of Experimental Physics, Uni-  
versity of Cambridge, Professor of Natural  
Philosophy, Royal Institution.*

## RECENT RESEARCHES ON THE GAMMA RAYS

[ABSTRACT]

It has long been known that some of the radio-elements emit a penetrating type of X-rays known as the  $\gamma$ -rays. It is clear that these radiations arising from the nucleus of the radio-active atom represent in a sense some of the characteristic modes of vibration of the nuclear structure. The wave length and quantum energy of many of the stronger lines in the complicated  $\gamma$ -ray spectrum have been determined by different methods with concordant results. It has been difficult to determine with certainty the origin of this radiation. It was at first supposed that it must arise from the motions of electrons in the nucleus, but in recent

years there has been a growing belief that the radiation is connected with the transition of an  $\alpha$ -particle or proton which forms part of the nuclear structure. It is not an easy matter to distinguish between the various hypotheses, since very little is known about the detailed structure of the nucleus. Fortunately, during the last two years, two different methods of attack on this problem have been developed. The first depends on an analysis of the groups of long range  $\alpha$ -particles which are emitted in small numbers from radium C and thorium C, and the other the analysis of the fine structure shown in the emission of  $\alpha$ -rays from certain bodies. It may be supposed that the emission of a  $\beta$ -particle during a transformation causes a violent disturbance in the resulting nucleus, some of the constituent  $\alpha$ -particles being raised to a much higher level of energy than the normal. These  $\alpha$ -particles are unstable and after a very short interval fall back to the normal level, emitting their surplus energy in the form of a  $\gamma$ -ray of definite frequency. According to the ideas of wave-mechanics, in this short interval there is a small chance that some of the  $\alpha$ -particles in the higher levels can escape from the nucleus. On these views, the escaping  $\alpha$ -particles represent the long-range  $\alpha$ -particles observed and the energy of the  $\alpha$ -particles gives the value of the energy level in the nucleus which it occupied before its escape. Following out these ideas, the long-range  $\alpha$ -particles which escape from radium C have been carefully analysed, using the new electrical methods of counting  $\alpha$ -particles.

Nine distinct groups of particles were observed, and the energies of  $\alpha$ -particles forming each

group were determined. The differences of energy between the various groups were found to be closely connected with the energy of some of the most prominent  $\gamma$ -rays in the spectrum, and, in general, the experiments gave strong evidence that the  $\gamma$ -rays had their origin in the transition of one or more  $\alpha$ -particles in an excited nucleus.

It has generally been supposed that in a radioactive transformation all the  $\alpha$ -particles are expelled with identical speed. This is certainly the case for most bodies, but Rosenblum found that the element thorium C emitted not one but five distinct groups of  $\alpha$ -particles. This discovery was made possible by making use of the great Paris electromagnet in order to bend the  $\alpha$ -particles into a semicircle. Gamow pointed out that the appearance of such a "fine structure" in the  $\alpha$ -ray emission should be accompanied by the liberation of  $\gamma$ -rays.

Owing to certain experimental difficulties, it is not easy to obtain a clear-cut decision on this point. Ellis concludes from his experiments that Gamow's view is correct, but Meitner from similar experiments reached an opposite conclusion. In view of this difference of opinion, I have made, in conjunction with Mr. Bowden, some experiments to throw light on this problem in another way. Recently Lewis and Wynn Williams found that the actinium emanation emitted two distinct groups of  $\alpha$ -particles differing in energy by about 340,000 volts. It was seen that this observation offered a simple method of testing the theory of Gamow. The emanation was carried by a current of air into a separate chamber and the emission of  $\beta$ - and  $\gamma$ -rays directly tested. It was found that the transformation of the emanation was

accompanied by a weak  $\beta$ -radiation, and a strong  $\gamma$ -radiation. The experimental results were in good accord with the theory, and thus showed that the presence of a "fine structure" in the  $\alpha$ -ray emission is accompanied by the emission of  $\gamma$ -rays. At the same time, the results afford strong corroborative evidence that the  $\gamma$ -rays have their origin in the transitions of an  $\alpha$ -particle in an excited nucleus.

It is of interest to consider how far these views can be carried into the region of the artificial disintegration of the elements resulting from the bombardment of certain light elements by  $\alpha$ -particles. In some of these disintegrations it is necessary to assume that the  $\alpha$ -particle can be captured in different energy levels, and that a  $\gamma$ -radiation is emitted as a result of the transition between the two levels. Penetrating radiations have, in fact, been observed in several cases when light elements are bombarded by  $\alpha$ -particles. Some of these cases are of peculiar interest.

### *The Radiation from Beryllium and the Neutron.*

In examining the artificial disintegration of light elements under the action of  $\alpha$ -rays, Bothe and Becker in 1930 noted that beryllium under  $\alpha$ -ray bombardment did not emit protons like boron or nitrogen, but gave out a weak radiation which was more penetrating in character than the  $\gamma$ -rays from radium. The absorption of this radiation in its passage through matter was later examined in detail by Mme. Curie-Joliot and M. Joliot and by Webster.

It is usual in experiments of this kind to employ active preparations of polonium on a metal disc as a source of  $\alpha$ -rays. This source is very con-

venient for the purpose, as the results are not obscured by the presence of  $\beta$ - and  $\gamma$ -rays, which are so freely emitted from other  $\alpha$ -ray sources such as radium C and thorium C.

In examining the absorption of this beryllium radiation by the ionisation method, Mme. Curie-Joliot and M. Joliot made the striking observation that hydrogen material, when exposed to this radiation, emitted swift protons. They suggested that if the protons gained their energy by a radiation recoil in a process similar to the well-known Compton effect, the quantum energy of the radiation must be of the order of 50 million electron volts.

J. Chadwick, using direct counting methods of great sensitiveness, found swift recoil atoms were liberated not only in the passage of the radiation through hydrogen, but also in other light elements, including helium, lithium, beryllium, carbon, air and argon. In a recent letter to "Nature" \* he pointed out that the results in this and other directions were difficult to reconcile with the hypothesis of a quantum of radiant energy of such high frequency. He suggested that the effects observed were not due to a  $\gamma$ -radiation at all, but to the liberation from the bombarded beryllium of a stream of swift uncharged particles or "neutrons."

The idea of the possible existence of neutrons, that is, of a very close combination of a proton and electron to form an uncharged nuclear unit of mass nearly 1, is not new to science, but it has been very difficult to find any definite evidence of its existence. Rutherford discussed the properties of such a neutron in the Bakerian Lecture before the Royal Society in 1920, and both the

\* "Nature," Vol. CXXIX, p 312. 1932.

late Dr. Glasston and Dr. Roberts made experiments in the Cavendish Laboratory to test whether neutrons were produced in strong electric discharge through hydrogen, but without success.

It is to be anticipated that a projected neutron would produce very little ionisation in its passage through matter, and would pass freely through the outer structure of atoms. A swift neutron should, however, indicate its presence by the recoil of an atomic nucleus with which it collided. This recoiling nucleus would spend its energy of motion in ionising the gas, and should thus be readily detected by its electrical effect, or by the trail of water drops it produces in a Wilson expansion chamber. In some respects, however, the effects produced by a neutron would be very similar to those due to a quantum of high frequency radiation, and careful experiment is required to distinguish between them.

A discussion was given on the present state of the experimental evidence on this important problem. The velocity of the neutron at the moment of its liberation is estimated to be about  $3 \times 10^9$  cm./sec., or about one-tenth of the velocity of light. By comparison of the velocity of recoil of different atoms, Chadwick finds that the mass of the neutron is about the same as that of the hydrogen atom. In addition, the velocity of recoil of a given atom falls off when the radiation is passed through increasing thicknesses of an absorbing material like lead. This is exactly the behaviour to be expected for the neutron, but not for a high frequency radiation.

Very valuable information on this problem can be obtained by photographing the effects due to the passage of this new type of radiation through



a Wilson expansion chamber. A number of such experiments have been made by N. Feather and P. I. Dee in the Cavendish Laboratory in association with Dr. Chadwick. For example, it is to be anticipated that the neutron would occasionally collide with the electrons in its path, and thus give rise to an electron track of maximum length corresponding to twice the velocity of the neutron. This is exactly analogous to the well-known production of  $\delta$ -particles by the passage of  $\alpha$ -particles through gases. Several such short electron tracks have been photographed by Dee which have about the right length, and for which it is difficult to suggest any other explanation. Feather has obtained photographs of more than a hundred recoil tracks produced in an expansion chamber filled with nitrogen. He has observed another very interesting effect. In addition to the straight recoil tracks, he has obtained photographs of a number of branching tracks which indicate that the nitrogen nucleus has disintegrated in a novel way. These branch tracks are believed to be produced by the recoiling nucleus and by some particle which is ejected from the struck nucleus. The identity of this latter particle has not yet been definitely established.

It will take time to analyse the results obtained, and to examine the effects produced in other gases. The peculiar properties of the neutron allow it to approach closely, or even to enter, nuclei of high atomic number, and it will be of great interest to study the effects of such collisions. It is, however, evident that this new radiation has surprising properties, and there is every promise that it may prove an effective agent in extending our knowledge of the artificial disintegration of elements

It will, for example, be of much interest to decide whether the neutron is captured in such disintegrating collisions, or whether it merely passes through the nucleus on which it has such a catastrophic effect.

Mme. Curie-Joliot and M. Joliot and Dee have independently noted that some swift electron tracks are observed in the expansion chamber. The exact origin and nature of these particles will require careful examination. It is possible that a  $\gamma$ -radiation is emitted from beryllium as well as the neutron. Mme. Curie-Joliot and M. Joliot found that the radiation from boron bombarded by  $\alpha$ -particles behaved similarly to that from beryllium. It is possible that other elements will also give rise to radiations of this kind.

Whatever may be the final explanation of the interesting facts observed, it is clear that if they are due to a quantum of radiation, we must relinquish the laws of the conservation of energy and of momentum in the production of this radiation and its interaction with matter. If we wish to retain these laws, the neutron hypothesis seems the only alternative. In any case it is evident that these new discoveries have opened up a new region of research which is of great interest and promise.

Slides were shown illustrating the production of protons and nitrogen recoil atoms due to the radiation of beryllium, using both electrical methods and the tracks in a Wilson expansion chamber. Photographs were shown of electron tracks and also of the branching tracks believed to be due to the disintegration of nitrogen nuclei by the action of the radiation. [R.]

Friday, June 3, 1932

SIR JAMES CRICHTON-BROWNE, J.P., M.D., LL.D.,  
D.Sc., F.R.S.

*Manager and Vice-President, in the Chair*

J. C. M'LENNAN, D.Sc., LL.D., F.R.S., M.R.I.  
*Professor of Physics and Director of the Physical  
Laboratory, University of Toronto*

ELECTRICAL CONDUCTIVITY  
OF METALS AT THE  
LOWEST TEMPERATURES

THROUGH the kindness of Colonel The Master of Sempill and Professor W. H. Keesom, who succeeded Professor Kammerlingh Onnes in the Directorship of the Cryogenic Laboratory in the University of Leyden, I am able to show my audience this evening some liquid helium and a persistent electrical current in a ring composed of lead in the superconducting state. This is the first time that liquid helium and an electric current in a metal in the superconducting state have been exhibited in England.

To-day a quantity of helium was liquefied by Professor Keesom in the Cryogenic Laboratory at Leyden. The helium was collected in a large glass Dewar flask supported in a second Dewar flask of glass containing liquid air. These two were supported in a third metallic Dewar flask,

also filled with liquid air. A small ring of lead, about 2.5 cm. in diameter and about 3 mm. in cross-section, was placed with its plane vertical in the bottom of the inner flask immersed in the liquid helium. At the temperature of liquid helium lead is superconducting, and in the present instance an electric current of about 200 amps. was induced in it by an external magnetic field.

Mr. Flim, Professor Keesom's assistant, carrying in his hands the Dewar flasks, was brought in a two-seater aeroplane by the Master of Sempill to the Aerodrome at Hanworth and thence by motor car to the Royal Institution.

The electric current was started in the lead ring at about three o'clock in the laboratory at Leyden. The flasks bearing the liquid helium and the ring traversed by the current were taken by motor car from Leyden to the aerodrome at Amsterdam where the aeroplane flight started. It took about three hours to fly from Amsterdam to Hanworth, and as it is now past nine o'clock we see that the electric current in the ring has persisted for over six hours. That an electric current is traversing the ring is made evident to all present by the effect its magnetic field exerts on the magnetometer on the table now before you.

It is over one hundred years since Faraday in collaboration with Sir Humphry Davy in the Royal Institution liquefied chlorine. This was an epoch-making event, for it led to a succession of similar experiments in the same laboratory in which one gas after another was liquefied. With the liquefaction of these gases lower and lower temperatures became available for research. With liquefied oxygen temperatures as low as  $-183^{\circ}\text{C.}$  can be reached. With liquefied nitrogen  $-196^{\circ}\text{C.}$ ,

with liquid hydrogen  $-262^{\circ}$  C., and with the large supplies of helium now available it is comparatively easy with the liquefaction of this gas to reach a temperature of  $-272^{\circ}$  C. or  $1^{\circ}$  Kelvin, *i.e.* one degree above the absolute zero.

The production of low temperatures by the use of liquefied gases has an important bearing on the solution of the problem of the passage of electricity through metals, a problem which for nearly one hundred and fifty years has remained unsolved either by the experimentalist or the theoretical physicist. Experiments by Dewar and Fleming\* in 1893 on the electrical conductivity of metals cooled to very low temperatures by means of liquefied gases, including air and hydrogen, yielded results represented by the curves shown in Fig. 1. These curves, it will be seen, suggest that the electrical resistances of all pure metals would vanish at the absolute zero of temperature.

In 1911, however, Kammerlingh Onnes at Leyden, while carrying out researches at low temperatures with the aid of liquefied helium, discovered that mercury, when cooled down and solidified with liquid helium, suddenly and abruptly at about  $4.2^{\circ}$  K. became what is now designated as a superconductor of electricity. At temperatures below  $4.2^{\circ}$  K. mercury offers no measurable resistance to the passage of a current. Currents of electricity started in a ring of mercury in the superconducting state will continue apparently undiminished in intensity while the metal is in that state. The duration of these persistent induced ring currents is limited only by the length of time the cooling agent, liquid helium, will last. Other metals that exhibit this superconducting

\* *Phil. Mag*, 5 S. XXXVI, p 271 [1893].

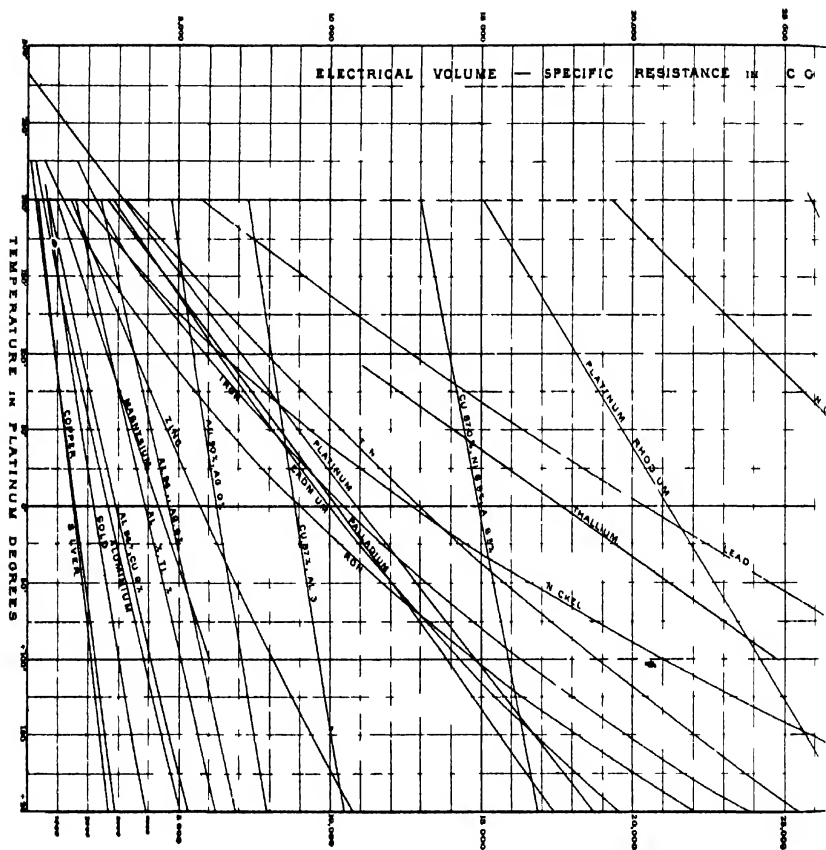
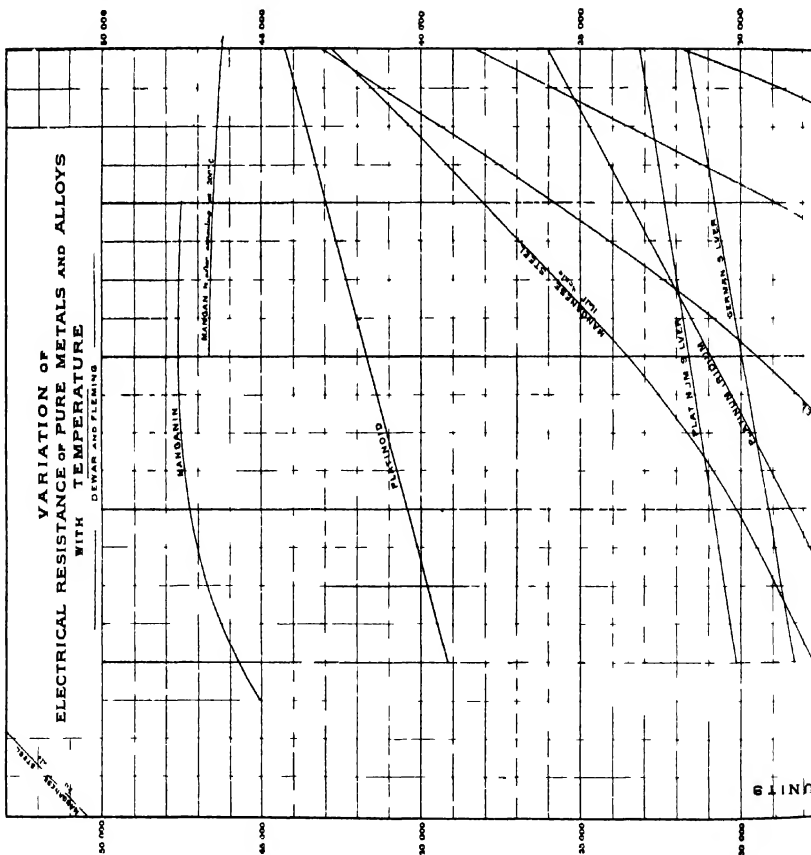


Fig 1—Curves showing the variation in electrical resistan

# VARIATION OF ELECTRICAL RESISTANCE OF PURE METALS AND ALLOYS WITH TEMPERATURE

DEWAR AND FLEMING



[By kind permission of the Editors *Philosophical Magazine*]  
 in temperature of wires made from different metals

property if made sufficiently cold are lead, tin, indium, gallium, thallium, tantalum, titanium and niobium. The transition temperature for the passing of a metal from the ordinary conducting to the superconducting state is not a constant but varies with the metal. For mercury it is  $4.2^{\circ}$  K., for lead  $7.2^{\circ}$  K., tin  $3.72^{\circ}$  K., tantalum  $4.5^{\circ}$  K., thallium  $2.39^{\circ}$  K., indium  $3.4^{\circ}$  K., gallium  $1.07^{\circ}$  K., and niobium  $8.2^{\circ}$  K. Some alloys and chemical compounds of the metals also exhibit the superconducting phenomenon. Copper sulphate, for example, does so, though neither of the constituent elements is a superconductor. The nitrides and carbides, borides and silicides of several of the metals, such, for example, as molybdenum, tungsten, tantalum, zirconium and niobium, are also superconducting at sufficiently low temperatures.

The addition of metals of the bismuth group to superconducting metals has been found, speaking generally, to raise their transition temperature. Bismuth added to lead raises the transition temperature from  $7.2^{\circ}$  K. to  $8.8^{\circ}$  K.; carbon raises that of niobium from  $8.2^{\circ}$  K. to  $10.5^{\circ}$  K. Gold alloyed with bismuth becomes superconducting at  $1.94^{\circ}$  K., whereas neither constituent alone becomes superconducting even at the lowest temperatures obtainable.

Recently the speaker, in collaboration with his associates, J. F. Allen and J. O. Wilhelm, made a study of various alloys of the Ag-Sn, Au-Sn, Au-Pb systems. Three outstanding features characterize the results. First, in alloys with the superconducting elements it was observed that gold and silver produce an effect on the transition temperature opposite to that produced



by bismuth, antimony and arsenic. When one observes alloys containing the latter metals one finds usually a pronounced elevation of the superconducting temperature, while in alloys with gold and silver one finds an equally pronounced depression of the superconducting temperature. Second, it was noted that a binary alloy system composed of a superconductor and a non-superconductor does not necessarily have a unique transition temperature. Third, it was found that with the alloy systems, Ag-Sn, Au-Sn, Au-Pb, the transition temperatures were higher for eutectic mixtures than for chemical compounds of the two metals constituting the alloys. The data compiled in Table I will serve to illustrate these points. The element silver and the compound  $\text{Ag}_3\text{Sn}$ , it will be seen, have not been found to be superconductors at any temperature reached up to the present.

TABLE I  
TIN-SILVER ALLOYS

Substance	Mixture	Percentage of tin	Transition T
Tin	Pure	100	3.76 K
Ag-Sn	Eutectic alloy	96	3.52 K
$\text{Ag}_3\text{Sn}$	Eutectic alloy	50	3.57 K
$\text{Ag}_3\text{Sn} + 3\text{Ag}$	Mixture	30	2.3 K
$\text{Ag}_3\text{Sn}$	Compound		
Ag	Pure		

The application of mechanical stresses such as those of torsion and tension raise the transition temperature of a superconducting metal, but the application of a magnetic field delays the appearance of superconductivity and causes it to appear in a metal at a lower temperature than normally.

If a metal in the superconducting state be subjected to a gradually increasing magnetic field, a critical field strength is reached when electrical resistance reappears in the metal. The strengths of the critical fields required for different superconductors vary; an alloy of bismuth and lead, for example, at  $1.2^{\circ}$  K. requires a magnetic field of 20,000 gauss to restore the property of electrical resistance, while metallic thallium at the same temperature requires a field of only 15 gauss.

Since the electrical resistance of superconducting metals is zero, no heat is produced when electrical currents are passed through them. Currents of high intensity can therefore be passed through superconducting wires of small diameter without melting them. Electric currents of more than 1000 amperes have been so obtained in wires of small cross-section. The factor that imposes a limiting value upon the current strength is the magnetic field set up in the wire by the current itself. A critical value is reached when resistance is restored to the wire by the magnetic field.

Owing to the fact that metals in the superconducting state have no electrical resistance, currents of electricity induced in rings of metals in this state will persist with undiminished intensity so long as the metals remain superconducting. So far it has been found impossible to detect with instruments of precision any diminution in the intensity of ring currents in superconductors even after the lapse of a period as long as thirteen hours.

Recently some experiments were carried out by the writer, J. F. Allen and J. O. Wilhelm on the intensities of persistent currents of electricity

induced in rings, having the same dimensions, of lead, tin and tantalum brought into the superconducting state by the use of liquid helium. The currents in the rings were induced by the magnetic field provided by electric currents established in a circular coil of wire placed in turn coaxial with and close to each of the superconducting rings. The results of these experiments are represented by the graph shown in Fig. 2. It was found that for the weaker magnetic fields equal changes of flux produced currents of equal magnitude in each of the three superconductors. The magnitude of the persistent current developed depends not on the substance of the superconducting ring but only on its dimensions and on the magnitude and form of the inducing magnetic field.

The case of tin is very interesting, since the values of the current in it agree with those of the current in the others only up to fields of about 25 gauss. For inducing fields higher than this the strength of the persistent current dropped off. Above this point, then, part of the ring must have been in a field, the strength of which had reached the critical value where resistance reappeared, that is, an inner layer of the ring must have become non-superconducting. As the field was increased above this point, one can suppose the outside superconducting portion of the ring became thinner and thinner until the whole ring became non-superconducting. Incidentally, this demonstrates that the magnetic field traversing the coil is not homogeneous but possesses a gradient from the axis of the coil to the edge of the coil itself. It may be this lack of homogeneity explains the discrepancy between the critical

field obtained by us (Fig. 2) and that obtained by Onnes,\* who found the critical field for tin at  $2.0^{\circ}$  K. to be in the neighbourhood of 200 gauss.

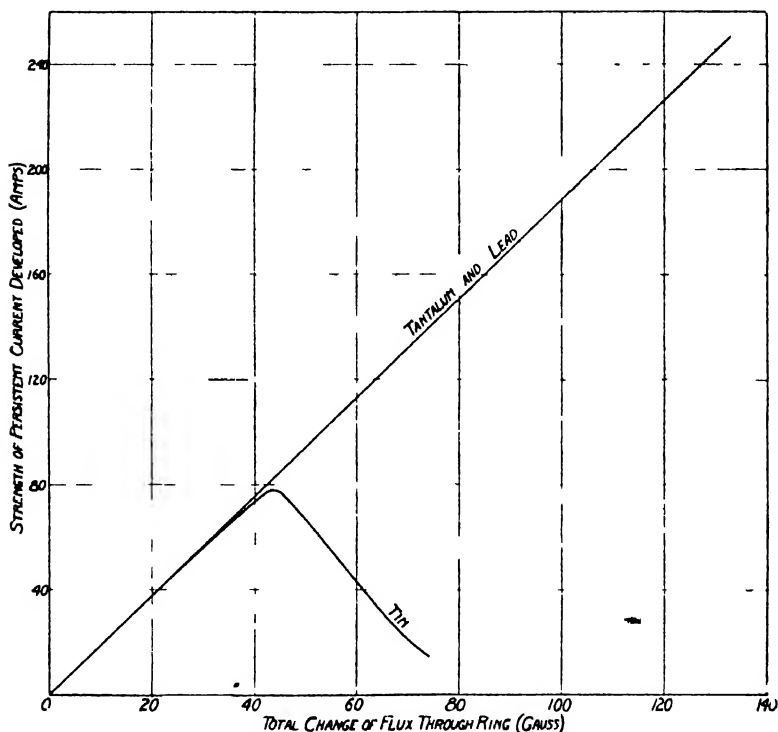


Fig 2 — Curves showing how the intensities of the currents induced in rings of tin, lead and tantalum in the superconducting state depend upon the total change of magnetic flux through the rings

The fact that the same flux engenders the same persistent current in different superconducting metals having the same size and form follows from an application of the equation

$$L \frac{di'}{dt} = \frac{dB_{\perp}}{dt} \quad \text{or} \quad i' = \frac{B_{\perp}}{L}.$$

For rings of the same dimensions, the self-inductances would be identical; and in the superconducting state the resistances of the three metals would be vanishingly small. These two factors produce the same magnitude of induced current in different superconductors.

Looking at the matter in another way, we see that the induced currents in the three superconductors must be the same since the magnetic field of the persistent current must be equal in magnitude and distribution but opposite in direction to the flux of the exciting field.

Since the discovery of the phenomenon of superconductivity in metals by Kammerlingh Onnes in 1911 researches in this field have been until recently almost invariably carried out by the use of unidirectional electric currents. No systematic attempt appears to have been made hitherto to investigate the phenomena of superconductivity with alternating electric currents of high, medium and low frequencies.

Some of the theories \* put forward to explain superconductivity suggest that an orientation of some kind is involved in the production of the superconducting state in metals. If this suggestion should prove to be correct, one would expect some modification of the phenomenon for currents of high frequency. It need only be mentioned that all "orientation" effects are considerably modified in an oscillating field with a time-period of the order of, or less than, the "time of relaxation" of such orientation. A well-known example is that of the dielectric constant which rapidly

\* For example, Sir J. J. Thomson, *Phil Mag*, 6 S. XXX, p. 192 [1915], and Richardson, *Phil Mag*, 6 S. XXX, p. 295 [1915]

diminishes in value for very high-frequency electric fields. As to "relaxation times," it will be recalled that in the case of ice, experimental evidence shows that the relaxation time is of the order of  $10^6$  sec. at  $0^\circ$  C. and rapidly increases as the temperature is lowered.\* It would not seem unreasonable then to expect to find "relaxation times" exhibited by metals in the superconducting state provided one used in one's experiments alternating fields of suitable and adequate frequencies. A short time ago an investigation was initiated in this direction by the speaker and through a set of researches carried out successively with the collaboration of a number of associates, *i.e.* Niven, Wilhelm, Burton, Allen, Smith, McLeod and others, the work recently culminated in the discovery that such metals as lead, tin and tantalum can be made to exhibit, when in the superconducting state, characteristic phenomena that point to their possessing "relaxation times" roughly of the order of  $10^7$  sec. or  $10^8$  sec.

#### ABSORPTION OF $\beta$ RAYS.

. In the first of these researches † the absorption of  $\beta$  rays by a thin sheet of lead was investigated when the lead was gradually cooled from a temperature a few degrees above to a few degrees below the critical transition temperature of  $7.2^\circ$  K. The  $\beta$  rays used were those emitted by mesothorium and the lead sheet had a thickness sufficient to absorb, at ordinary room temperature,

\* Errara, *J. Phys.* (6) v. p. 304 (1924); J. Granier, *Compt. Rend.* clxxix, p. 1314 (1924); Debye and Wentsch, see "Polar Molecules," by Debye, p. 102, pars. 20 *et seq.*

† M'Lennan, McLeod and Wilhelm, *Trans. Roy. Soc. Canada* 3 S. XXIII, Sect. III, p. 269 [1929].

50 per cent. of the  $\beta$  rays issuing from the mesothorium. In these experiments no measurable variation or discontinuity was detected in the absorption coefficient as the temperature of the lead was lowered through the critical value  $7.2^\circ$  K. The high velocity electrons from the mesothorium apparently encountered just as much resistance in their passage through the lead with the latter in the superconducting state as when the lead possessed the normal conductivity exhibited at the higher temperatures. This investigation gave definite proof that although resistance in the superconducting state is zero, or a very low value for currents carried by slow-moving electrons, it is not zero but maintains a normal value for currents carried by high-speed electrons.

Looking at the matter in another way this result indicates, if the De Broglie wave equation  $p = \frac{h}{mv}$  applies, that lead at the lowest temperatures cannot exhibit superconductivity when subjected to alternating electric fields with frequencies of the order of  $10^{21}$  per sec.

#### PHOTOELECTRIC AND LIGHT ABSORPTION EXPERIMENTS

In a second series of experiments \* thin films of lead were deposited on plates of glass and of quartz, sometimes by cathode spluttering and at other times by vaporization of metallic lead. These films were subjected to a series of decreasing temperatures commencing a few degrees above

\* M'Lennan, Hunter and McLeod, *Trans. Roy. Soc. Canada*, 3 S. XXIV, Sect. III, p. 3 [1930], M'Lennan, Burton, Pitt and Wilhelm [Footnote], *Phil. Mag.*, 7 S. XII, p. 708 [1931], M'Lennan, Smith and Wilhelm, *Phil. Mag.*, 7 S. XII, p. 835 [1931].

$7.2^{\circ}$  K. and ending at the temperature of liquid helium  $4.2^{\circ}$  K. The photoelectric effect and the absorption of visible light were in turn investigated with these films and measurements were taken approximately by steps of a fraction of a degree as the temperatures of the films were lowered. In these experiments no measurable discontinuity was observed in the results of our measurements on the photoelectric effect, nor in the results of those on the coefficient of absorption of the light waves when the lead films traversed were passed through the transition temperature of  $7.2^{\circ}$  K. These results were taken therefore to indicate that superconductivity with lead is a phenomenon that cannot be exhibited when electric fields alternating with a frequency approximately equal to or greater than  $10^{14}$  per second are used.

It is clear, however, since superconductivity can be brought into evidence by the use of unidirectional fields, *i.e.* with fields of zero frequency, that there must exist some critical alternating field with a frequency between zero and  $10^{14}$  per second, by the use of which superconductivity should just be detectable.

#### EXPERIMENTS WITH ELECTRIC FIELDS OF RADIO-FREQUENCIES

Through the development which has taken place in recent times it is a comparatively simple matter to arrange combinations of oscillating valve systems capable of providing alternating electric fields with frequencies as high as  $10^7$  or even  $10^8$  per second. Some experiments were therefore made with radio fields having frequencies approximating to  $10^7$  cycles per second and corre-



sponding to a wave-length of about 30 metres. With fields of this frequency it was thought that the phenomenon of superconductivity might appear with lead at a lower temperature than  $7.2^{\circ}$  K., might even be only partial, or might not appear at all. The experiments \* and apparatus used together with the theory applicable have been fully described elsewhere and are therefore only briefly referred to here.

A resonant circuit was constructed consisting of a coil of the wire under investigation which was wound on a former in series with a condenser mounted on the same former. The entire electrical circuit was made of the metal under investigation. The resonator used in the first experiments was made of lead. The lead plates of the condenser were kept at the proper distance apart by fibre washers on the central spindle. This resonator, in the experiments, was kept in the Dewar (unsilvered) flask in which the liquid helium or gaseous helium of a low temperature was produced. Temperatures were measured with helium gas thermometers or were deduced from the vapour pressure of the liquid helium.

A reactance method was used and the plate and grid coils of the oscillating system were placed, properly screened, external to the thermos flask containing the resonator circuit and immediately below it. The magnitudes of the currents induced in the resonance coil were measured by their reaction upon the oscillations in the generating circuit as indicated by the plate current of the latter. Measurements made in this way enabled

\* McLennan, Burton, Pitt and Wilhelm, *Phil. Mag.*, 7 S. XII, p. 707 [1931]; *Trans. Roy. Soc. Canada*, 3 S. XXIV, Sect. III, p. 191 [1931]; *Nature*, CXXXVIII, p. 1004 [1931]; and *Proc. Roy. Soc. A*, CXXXVI, p. 52 [1932].

one to deduce the value of the resistance corrected for skin effect of the wire in the resonance circuit when fields of different frequencies were used at various selected low temperatures.

### EXPERIMENTS WITH LEAD WIRES

In our first experiments a lead wire and a lead condenser were used as the resonating circuit and fields with a frequency of 11 million cycles per second were applied to it. In preliminary experiments with direct current the lead wire in the resonance circuit became superconducting at  $7.2^{\circ}$  K., but no evidence of superconductivity was obtained at this temperature when the alternating high-frequency field was used. The temperature of the lead resonance coil was then reduced to  $5^{\circ}$  K., and at this temperature it was found, with a field of  $10^7$  cycles per second, to be in the superconducting state. It was difficult to measure temperatures with great exactness between  $4.2^{\circ}$  K., the temperature of liquid helium, and  $14^{\circ}$  K. approximately the lowest temperature obtainable with liquid hydrogen. Experiments with lead wires were therefore not pursued further, but in their place resonance circuits of tin and of tantalum were successively used. It was more convenient to work with these two metals as their transition temperatures were between the boiling-points of helium and hydrogen. By immersing the resonance circuits in liquid helium and lowering or raising the vapour pressure above the helium it was quite practical to carry each of these circuits through a relatively considerable range above and below their critical transition temperatures. The method possessed the advantage that it was a highly sensitive one,

for a change in the vapour pressure of helium of 50 mm. of mercury corresponded to a change of one-tenth of a degree Kelvin within the range of temperature covered by the experiments.

### EXPERIMENTS WITH TIN WIRES

In some preliminary experiments with a coil of tin wire drawn to a diameter of 0.3 mm. it was found that with direct currents the resistance of the coil began to decrease abruptly at  $3.76^{\circ}$  K. and disappeared completely at  $3.70^{\circ}$  K. Experiments with the same coil with currents of frequency  $1.1 \times 10^7$  per second gave for the corresponding temperatures  $3.67^{\circ}$  K. and  $3.61^{\circ}$  K., *i.e.* superconductivity did not begin to appear until a temperature was reached that was below the one at which it was complete in the case of the direct current experiments. Further experiments

TABLE II  
RESULTS OF EXPERIMENTS WITH TIN

Wave length	Frequency $\omega \times 10^7$	Starting point		Vanishing point	
		Press	Temp	Press	Temp
metres		mm	K	mm	°K
$\infty$ (D.C.)	0	455	3.770	450	3.700
$\frac{144}{\text{diameter } 0.038}$	0.208	460	3.720	424	3.66
$\frac{46.5}{\text{diameter } 0.060}$	0.645	441	3.650	422	3.65
$\frac{27.2}{\text{diameter } 0.038}$	1.10	435	3.665	408	3.61
$\frac{26.5}{\text{diameter } 0.060}$	1.14	435	3.665	405	3.61
$\frac{18.7}{\text{diameter } 0.060}$	1.61	425	3.650	396	3.59

with higher frequencies revealed depressions of the critical transition temperature increasing in amount with the frequency. The results of a set of experiments carried out with extreme care, with tin wires 0.038 cm. and 0.060 cm. in diameter with fields having frequencies between  $0.2 \times 10^7$  and  $1.61 \times 10^7$  cycles per second, are given in Table II.

The results for the different frequencies are shown on the graph in Fig. 3, in which the pressures and corresponding temperatures at which the superconductivity started and "finished" are plotted against the frequency of the currents in the metal.

#### EXPERIMENTS WITH TANTALUM

In order to establish that the frequency disturbance of superconductivity observed with lead and with tin was a property of superconductors in general, experiments with other metals were considered. Tantalum fulfilled best the conditions for accurate measurement, as its critical temperature, for direct currents, approximately  $4.38^\circ \text{K.}$ , may be obtained by raising the vapour pressure over liquid helium to 900 mm. of mercury.

The frequency of  $1.14 \cdot 10^7$  was used, as this had given the most easily reproducible results in the experiments with tin. Highly purified tantalum was available in the form of wire, of diameter 0.0254 cm., and the condenser plates were cut from a sheet of tantalum of thickness 0.043 cm.

The resistance of the tantalum wire used in the resonator system was, at room temperature, greater than that of the tin coils used, as the

diameter of the wire was much less. The resistance also decreased much less than that of the tin as the temperature was lowered, the ratio

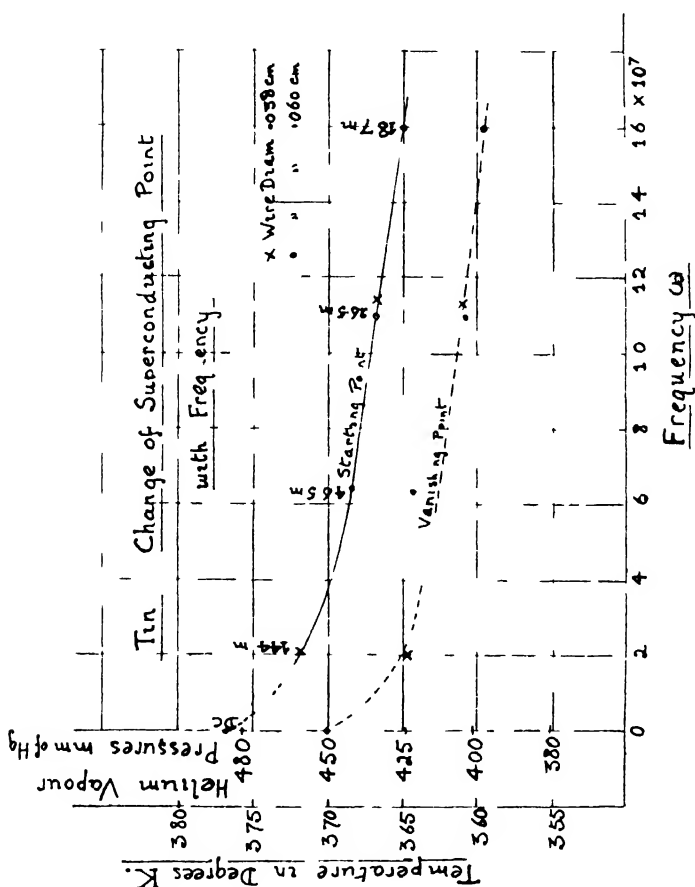


Fig 3—Curves showing how the superconducting transition temperature for a tin wire varies with the frequency of the alternating current used

$R/R_0$  for direct currents, just above the superconducting point, being 0.07 instead of 0.002 for tin and 0.001 for lead. The progress of the

measurements with tantalum is shown in Table III, and illustrated in Fig. 4. The abrupt fall of resistance did not begin until a pressure was

TABLE III

TANTALUM  $\omega$  11.4  $\times 10^4$ 

Temp °K	Pressure, mm Hg	Peak $p$ in cm scale	R R <sub>0</sub>	R R <sub>0</sub>
300		2.20	1.00	1.00
70		3.75	0.54	0.305
70		1.15	0.27	0.094
125		2.45	0.27	0.094
70		2.25	0.295	0.110
440	917	3.40	0.24	0.079
4355	877	3.40		0.079
434	855	3.40		0.079
4305	838	3.30		0.056
427	817	3.25		0.058
425				0.057
425	805		1.30	0.051
425	799		1.35	0.056
425	797	3.30		0.081
4245	794		1.35	0.057
4235	785		1.30	0.075
4225	778		1.40	0.074
422	777	3.50		0.069
422	773		1.50	0.061
421	769		1.55	0.0655
420	765	3.70	1.60	0.061
4195	755	50		0.037
419	753		2.00	0.036
418	745	4.90		0.033
418	744		2.10	0.027
4165	735	5.45		0.0195
415	725	6.35		0.017
415	724		2.90	0.014
4135	715	7.40		0.005
4135	714		3.40	
412	705	Too sharp		

reached only just greater than the atmospheric pressure, and to reach the point where the superconducting state was complete the pressure over the helium had to be reduced below that of the

atmosphere. The results of all experiments with direct currents with the same coil are given in Table IV, and a curve representing them is also shown in Fig. 4. The fall in resistance, it will be noted, was very abrupt. This indicates that the sample of tantalum wire used was of very high purity.

From the curve in Fig. 4 and the results in

TABLE IV  
TANTALUM D.C.

Pressure, mm Hg	Kelvin temperature	$R/R_0$
—	300	1.000
—	85	0.722
—	11	0.0726
—	7	0.0725
904	—	0.0726
900	4.38	0.0726
897	—	0.0700
896	—	0.0600
892	4.37	0.0200
888	—	0.0200
882	4.36	0.0100
871	—	0.0030
860	4.34	0.0020
858	—	0.000

Tables III and IV, one sees that with the field of  $1.14 \times 10^7$  cycles per second there was a very definite depression of the critical temperature. It amounted to about  $0.22^\circ$  K., and corresponded to a drop in the vapour pressure from 900 mm. to 800 mm. The apparent rise in the resistance to high-frequency currents just before the fall to superconductivity may be due to experimental error, which was much greater in this region,

than for the smaller values of the resistance. The transition to the superconducting state with the

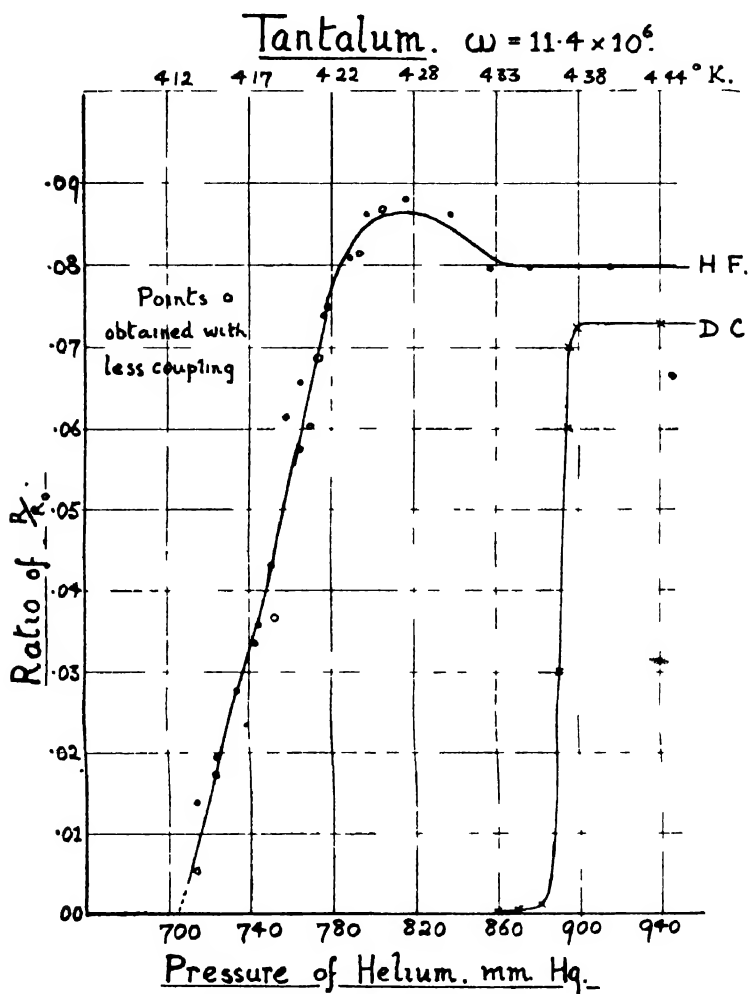


Fig 4 —Curves showing the variation with temperature of the electrical resistance of tantalum wire when investigated with (1) direct currents and (2) high-frequency currents

alternating field as the curves show was not nearly so abrupt as it was with the direct currents.



## DISCUSSION OF RESULTS

The experiments have established, first, that for currents of frequency  $10^7$  per second there is an abrupt fall in the resistance of a superconductor corresponding to the abrupt disappearance of resistance for direct currents, when the temperature falls below a critical value. The methods of measurement and the complications that are unavoidable with these high frequencies made it impossible to find how nearly zero the high frequency resistance became in the superconducting state, but it fell to a value certainly less than, in the case of lead, one-hundredth of its original value within a range of temperature of a fraction of a degree Kelvin. Results of some reliability were obtained, for tantalum, for the way in which the resistance decreased after the critical temperature was reached, and it was found that the slope of the curve was much less than for the direct currents, *i.e.* the transition to superconductivity was not so abrupt.

Secondly, it has been established that the critical temperature at which the phenomenon occurs is lower for the high-frequency currents than for direct currents in the same specimen.

The experiments with different amounts of coupling of the generator to the tin resonator coils proved that this depression of the critical temperature was not dependent upon the magnitude of the high-frequency currents in the metal, and was therefore attributable neither to the heating of the coil above the surrounding helium nor to the effect of the magnetic field of the currents. Experiments with wires of different sizes but with the same frequency showed that the depression was not a direct function of the

skin effect. It must then be a function of the frequency of the currents in the metal alone.

Further, the amount of the depression of the temperature increases with increase of frequency in the manner shown by the graph Fig. 2. Though the curve is continued by the dotted line to reach the axis of zero frequency at an oblique tangent, it might be expected that the true tangent at the axis would be horizontal, the departure beginning at some frequency of the order of  $10^5$  or less. It would be desirable to settle this point experimentally, but the depression of temperature would in either case be so small in this region that a definite conclusion would be difficult to obtain.

The curve appears to become linear at the higher frequencies, and if the extrapolation to the zero of the temperature scale be made on this supposition a frequency of the order of  $10^9$  is reached. This is true even if a parabolic law is fitted to the experimental points. The conclusion, if this extrapolation is justified, is that for frequencies greater than this, which corresponds to a wave-length of the order of 30 cm., the superconducting state does not exist. In support of this is the fact that no evidence of an abrupt change corresponding to superconductivity has been observed with light waves, experiments so far having given a negative result.\*

The disturbance of the superconducting point by frequency of the applied field must then be added, with its theoretical implications, to the other known disturbing effects that change the critical temperature, as that of a magnetic field, of tension, and of alloying with foreign metals.

\* M'Lennan, Hunter and McLeod, *Proc. Roy. Soc. Canada*, 3 S. XXIV, Sect. III, p. 3 [1930].

It is well known that all "orientation" effects, that is, phenomena which involve vector quantities, are considerably modified in high frequency fields provided the frequency is sufficiently high, and it might be expected that the corresponding relaxation for a metal lattice at very low temperatures would be comparable to an oscillation period lying well within the radio-frequency range.

The decrease in the magnetic permeability as the frequency is increased has recently been established by the experiments of Arkadiew \* and Wien.† In this case the modification does not become appreciable until a frequency corresponding to a wave-length of 5 metres is reached, *i.e.* the relaxation time is of the order of  $10^{-8}$  seconds.

The introduction of high frequency fields instead of static fields usually modifies the mathematic analysis by the introduction of a factor

$\frac{1}{1+j\omega\tau}$ , where  $\omega$  is the frequency and  $\tau$  the relaxation time, *i.e.* of an amplitude factor  $\frac{1}{(1+\omega^2\tau^2)}$  together with a phase difference. If inertia has to be considered as well as frictional forces, the factor takes the form

$$\frac{1}{[(1-a\omega^2)^2 + \omega^2\tau^2]^{\frac{1}{2}}}$$

In a recent theory, due to L. V. King,‡ which develops the theory of J. J. Thomson,§ the superconducting state is connected with the existence

\* *Ann. Physik*, vol. XI, p. 406 (1931).

† *Ann. Physik*, vol. XI, p. 423 (1931).

‡ Not yet published.

§ *Phil. Mag.*, 6 S. XXX, p. 192 [1915].

of a permanent state of dielectric polarization in the metal lattice, as would be predicted from the ordinary equations for the polarization under an applied field, if the polarizability became great enough with fall of temperature. In this state the internal field of the oriented dipoles is sufficient to hold them so oriented against the tendency of thermal agitation to re-orient them at random. It seems to us that with higher frequency fields, with the introduction of a factor such as given above, the polarizability becomes less, and a lower temperature has to be reached before the condition for permanent polarization is fulfilled. The simple theoretical treatment, however, does not give for the variation with frequency the form of the curve found experimentally.

The analogy of superconductivity with ferromagnetism and of the superconducting critical temperature with the Curie point, is given additional emphasis by these experiments, for in 1914 J. R. Ashworth \* found that an alternating field produced a lowering of the Curie point. Confirmatory experiments have not been reported. It is to be hoped that superconductivity will prove to have an explanation along similar lines to the theory of ferromagnetism, in which case much of the work of Heisenberg might be taken over into the new field. When results have been obtained for more metals than the three already investigated, a correlation between the magnetic disturbance and the frequency disturbance of the critical point may be possible. At present we know that the latter effect is greater in tantalum than in tin, and probably greater in lead than in

\* *Phil Mag*, 6 § XXVII, p 357 [1914], *Nature*, vol CXXVIII, p. 1003 (1931).

either. The magnetic disturbance is greater in lead than in tin ; that of tantalum has not been investigated.

The data so far obtained are far too incomplete to justify any attempt at a quantitative explanation, but a new road of attack upon the fundamental problem of superconductivity seems to be opened up by the discovery of the frequency disturbance.

In conclusion, I should like to draw attention to some experiments recently made by Silsbee, Scott, Cook and Brickwedde \* in Washington. In these they found that superconductivity could be obtained by means of currents alternating with frequencies between 60 per second and  $10^7$  per second. Their experiments, however, were apparently not designed or arranged to reveal the lowering of the critical temperature of transition observed in our experiments.

[J. C. M.]

\* Silsbee, Scott, Cook and Brickwedde, *Physical Review*, 2 S. XXXIX, p. 379 [1932].

Friday, January 20, 1933

SIR ROBERT ROBERTSON, K.B.E., M.A., F.R.S.,  
*Treasurer and Vice-President, in the Chair*

SIR WILLIAM BRAGG, O.M., K.B.E., M.A.,  
D.Sc., F.R.S., M.R.I.  
*Fullerian Professor of Chemistry*

## THE CRYSTALS OF THE LIVING BODY

It is obvious that the atoms and molecules of a living body are not thrown together in a haphazard fashion. There is in the first place a certain preferential disposal of the various kinds of atoms. While carbon, oxygen, hydrogen are widely and plentifully distributed throughout the body, the bones and teeth are comparatively rich in phosphorus and calcium, the hair contains sulphur and nitrogen, and so on. But these and other special occurrences are not enough to serve the body's purposes. There is a greater differentiation in the distribution of the molecules into which the atoms are grouped. There are, for example, many kinds of protein molecules which have their several parts to play as constituents of the different organs, and help to endow each organ with its peculiar function. But again this is not enough. There is a further requisite, namely order in the arrangement of the mole-

cules ; which gives directive action to the various composite masses. A hair for example is largely composed of a species of the proteins known as the keratins. These are long narrow molecular arrangements which we shall presently consider more in detail. The molecules are fastened together, somewhat loosely it would seem, into little bundles, in which the molecules all point nearly in the same direction. The bundles are so disposed that this direction is nearly the same as that of the axis of the hair.

This order in the arrangement of the long molecules would seem to us, now that we have discovered it, to be in accordance with what we might have expected. The long molecules are an important part of the hair, and indicate a disposition of its components which must give to it directional properties. The hair grows in a particular direction to which also its various mechanical properties are related. If the molecules lay in all directions, there would be no reason why the hair should be long, narrow, flexible and yet strong. All growth in Nature implies extensions in particular directions ; function is connected with orientation, and there can be no orientation without method in the molecular arrangements. For it has never yet been found that a process in a living body moves in contradiction to the laws of physics and chemistry as observed in the laboratory. This does not of course imply that any artificial arrangement of atoms and molecules has ever been endowed with life. A mass of molecules so indiscriminately arranged that no particular direction can be distinguished from any other, cannot be expected, even though it is part of a

living body to extend and grow in one direction more than in another.

We have taken a hair as an example, but other parts of the body would have served equally well. Nerves, muscles and tendons all possess arrangement ; the bones are not merely shaped externally as an engineer would shape them, but show also in the internal arrangement of their molecules an orientation for a definite purpose which the engineer must envy.

Clearly, if arrangement of the molecules is so necessary to enable the body to function and to live, the actions of the body cannot be fully understood without taking it into account. The new methods of analysis by radiation of very short wave-length, including we may now say electrons as well as X-rays, have provided us with means of examination of structure which are of much greater power than any that we possessed previously. These latter have been indeed very few and indirect. Furthermore, catalytic actions depend on the arrangements of the atoms and molecules on the surface of the catalysing solid ; but though this fact may have been appreciated, the details of the arrangement have been out of reach. In fact the new methods open up possibilities which are also new.

Our chemical methods, it must be pointed out, do not reveal the nature and details of molecular arrangements. When we employ them for the analysis of a material we begin by pulling the material to pieces and so destroying that very arrangement of molecules which we should be glad to examine. We knock the house down, and discover the numbers and natures of its components ; so many bricks, so many slates, so



many planks and so on ; but we have lost the plan of the house.

We must differentiate between the arrangement of atoms in the molecule, and of the molecules with respect to one another. The former has long been the study of the chemist, and especially of the organic chemist : there is no need to describe the extent to which it has been carried successfully. In such studies the molecules are free and approachable from all round, being either the constituents of a liquid or in solution in a liquid. A liquid has no permanent directional properties except, possibly, at its surface. On the other hand, the mutual arrangement of the molecules in the solid is fundamentally concerned in those directive properties which are characteristic of the solid ; it is this arrangement which is now open to our examination.

As illustrations of the effects of mutual arrangement among the molecules we may first consider the case of two soap bubbles which may be rubbed together not too violently—without coalescing. The material of the film is contained between two surface borders of long chain molecules which are arranged so as to present their methyl ( $\text{CH}_3$ ) terminals to the outside of the film. Thus a “methyl face” of one bubble rubs against a similar face on the other. There is very little action between methyl groups and so the films remain separated. The active ends of the molecules are all turned inwards and so are kept out of each other’s reach.

The solid crystal naturally gives the readiest examples of molecular arrangement, since the arrangement is the cause of the crystalline form.

Every face presents only some selected part of a molecule to the external world. Zinc-blende may be looked on as an assemblage of molecules composed each of one atom of zinc and one of sulphur, all lying parallel to one another. Two opposing faces, both perpendicular to the direction in question, and forming parts of the crystal boundaries, differ in their behaviour because one is associated with zinc atoms in the same way as

the other with sulphur. It is well known that if the crystal is heated one such face is positively electrified and the other negatively. There are four such directions in each crystal of zinc-blende and four corresponding methods of picturing the assemblage of molecules.

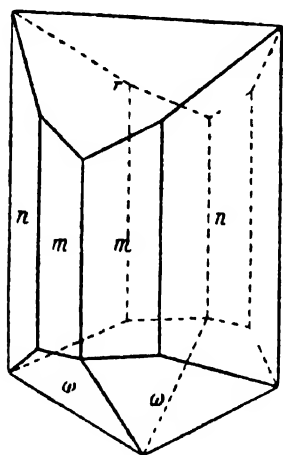


FIG. 1.—Resorcinol

Resorcinol [Fig. 1.] possesses the same property to a high degree. The molecule is unsymmetrical being a benzene ring in which two of the hydrogens at points  $120^\circ$

a-part are replaced by hydroxyl (OH) groups. The arrangement of the molecules in the crystal has not been determined exactly but we know that it is at any rate insufficient to give the crystal a high order of symmetry. The symmetry is certainly higher than that of the molecule itself as is usually the case. There still remains a strong polarity which is revealed by the form of the crystal. The upper end of the crystal in the figure is very different from the lower; the faces that form naturally at one end are not those which form at the other.

The polarity can be very simply demonstrated by suspending a couple of crystals in liquid air, whereupon they develop opposite electrical charges at their ends, so strong that the two behave to one another like small magnets. The strong electrification of resorcinol and similar bodies is sometimes used to clear liquid air of foreign particles.

The behaviour which is thus exhibited is the behaviour of the unit of pattern in the crystal. The unit can be shown by the X-ray methods to contain four molecules : arranged in a way which, as the term "unit of pattern" implies, is repeated indefinitely in the structure of the crystal. Mere multiplication cannot alter the properties of the crystal. whatever is true of the crystal as a whole is true of the single unit as it lies embedded in the crystal. That does not mean, necessarily, that the single unit would behave in the same way as it does in the crystal if it were free of its environment.

This is an extremely important point. We obtain from observation on the crystal information respecting the properties of a certain small company of molecules, generally not more than two, three or four. These properties are various, magnetic, electric, optical, thermal and so on. If we determine the arrangement of the molecules in the unit, and of the atoms in the molecule, we may correlate properties and arrangements and so contribute to the solution of one of the great problems of physics, viz., the connection between the properties of a substance and the atoms of which it is built. Conversely, knowing relations between the properties of one or more unit and the details of their structures, we may

use our knowledge for the determination of the structures of other units by the examination of the properties of the crystals of which such other units form part.

To sum up what I have said so far, the positions of the various atoms in the molecule determine the characteristic of the molecule: this is well

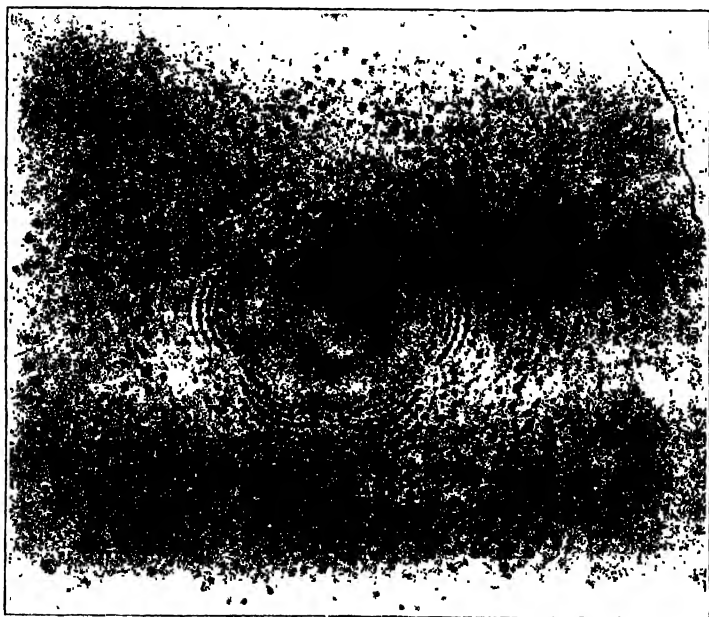


FIG. 2.—Kaliophilite.

known and has been widely studied. The positions of the molecules in the solid are equally important, especially if there is any regularity in their arrangement, in other words, if there is any attempt at crystallisation. In a living body there must be arrangements of various kinds to various extents. We want to know what these arrangements are and their effects.

The X-rays demonstrate to us any such arrangements. It is now well known that a pencil of X-rays which passes through any substance where molecular arrangement exists gives some sort of diffraction pattern, which may

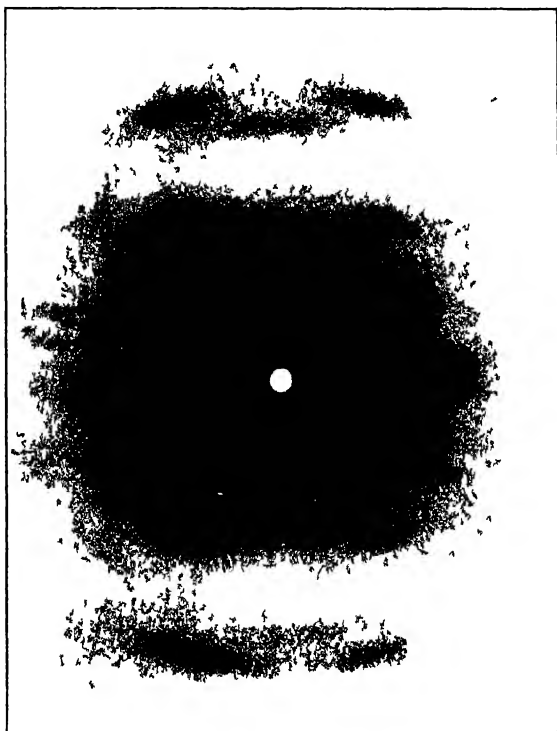


FIG. 3 Silk

be examined photographically or electrically. From the character of the pattern information can be obtained as to the nature of the arrangement. When there is much arrangement and great regularity the pattern is sharply defined. As an example, we may take the photograph of the mineral kaliophillite [Fig. 2] obtained by

F. A. Bannister of the British Museum. When the arrangement is less regular, the photograph is less definite. When the first photographs were obtained from silk and wool, nerve and muscle, they were in comparison exceedingly vague and it seemed that it would be difficult to make any useful deductions from them. However, both technique and skill in interpretation have

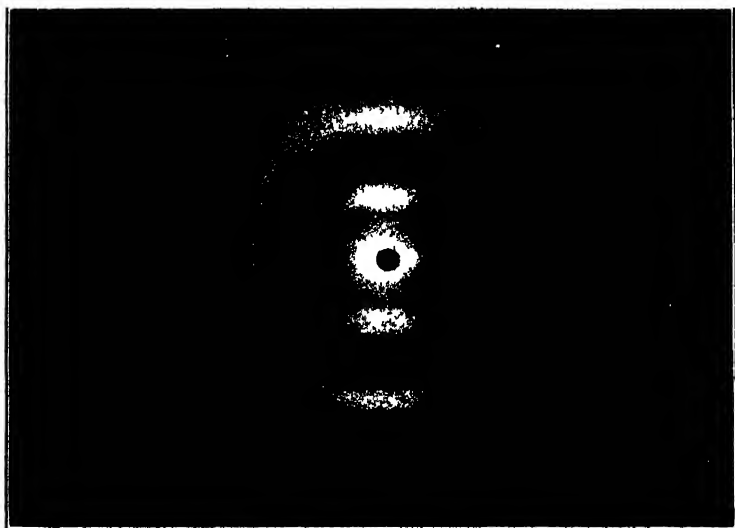
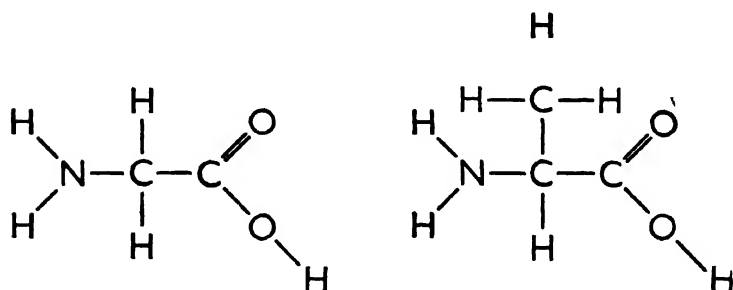


FIG. 4 —Sea-Gull's Quill.

increased materially and conclusions can now be drawn which are of great interest. The two photographs of proteins in Figs. 3 and 4 were obtained respectively from silk and from the quill of a sea-gull's feather. These are due to W. T. Astbury and Miss Marwick. The detail is sufficiently pronounced to give valuable information to the experienced observer.

In the first place, it is clear that there must be quite a considerable amount of arrangement in

both cases. The silk is largely composed of a protein known as fibroin. It is remarkable that similar photographs are obtained from a great number of proteins, drawn from different sources ; there is in fact a characteristic protein photograph which implies that there are elements of structure common to protein forms. The second photograph is an example of the diffraction pictures obtained from a peculiar class of proteins



Glycine.

FIG 5.

Alanine

known as the keratins ; their connection with the main body has recently been beautifully demonstrated by Astbury, as we shall see presently.

It has continually happened during the recent development of X-ray analysis that its first results have been confirmations of the conclusions of the organic chemist, and have been followed immediately by closer definitions and fuller knowledge. The chief feature of the structure of proteins has been supposed, on chemical grounds, to be a chain-like arrangement of certain complicated molecules known as amino-acids. These bodies may be obtained in the laboratory by breaking up the natural proteins. There are many kinds of them, and they can be separated and examined in detail. Two of the

simplest are glycine and alanine, which may be represented as in Fig. 5.

They are characterised by the presence of an amino-group  $\text{NH}_2$  on one side of a certain carbon atom and of a carboxyl group  $\text{COOH}$  on the other. The one has a positive character, the other a negative : the two groups have not only a general attraction for one another, but can also be made to combine in the manner shown in Fig. 6.

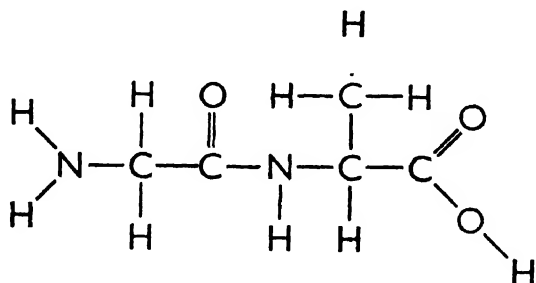


FIG. 6. Glycine and Alanine.

Two hydrogen atoms and one oxygen have dropped out. Willstatter supposed that such combinations could take the place in regular alternations of the two amino-acids, thus forming a chain of indefinite length.

Now alanine and glycine can be obtained from the decomposition of natural silk. If this regular structure is the cause of the X-ray photograph of silk, the numerical details that can be obtained from an examination of the photograph must fit in with the structure proposed by the chemist. This is remarkably verified. Previous X-ray work has shown that a chain composed of two carbons and one nitrogen in regular succession would probably take the zig-zag form well known



as a characteristic of long chain compounds. Fig. 7 shows how the silk protein would be represented.

From the X-ray analysis of many organic compounds we have learnt the dimensions of the atoms of carbon and nitrogen, and we can assert that the distance along the chain at which the pattern (two carbons and one nitrogen) repeats itself should be about 3.6 Angstrom units. Now the interpretation of the X-ray picture, though

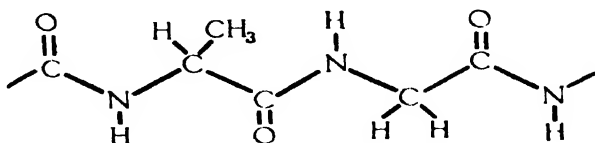


FIG. 7.—The Fibroin Chain.

hazy in some respects, is exceedingly precise in one at least. It shows that some arrangement exists along the fibre, based on a pattern which repeats itself at intervals of 3.5. The coincidence is striking. The X-rays show not only that there is arrangement among the molecules in the silk, but also that there is agreement with chemical theory as to the existence of a repeat in each chain. They show also that the chains—this also is one of the details which can be examined in the picture—are arranged more or less parallel to one another and to the direction of the fibre. This is the sort of arrangement which we should expect.

Silk fibroin is one of the simplest of the proteins. There are innumerable other possible combinations, because there are many different amino-acids and kindred bodies which can be strung on to the chain in various ways. There is for

instance cystine [Fig. 8.] which clearly can be inserted into the chain by either of its ends. This group contains the sulphur which occurs in hair.

To return now to the keratins which, as I have said, do not give the same diffraction pattern as silk and other proteins. Hair, feathers, horn and the like give photographs which are comparable with each other. Astbury\* has made the surprising discovery that a hair when stretched

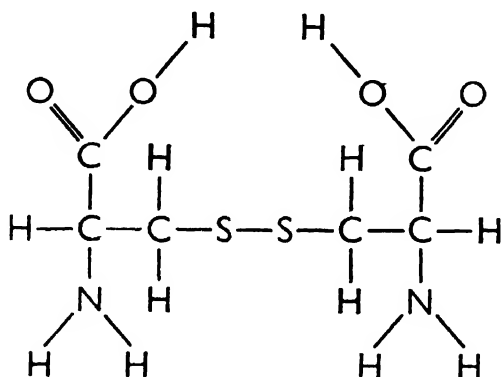


FIG 8. Cystine

gives a picture resembling that of silk. The stretching alters the arrangement of the molecules. If the hair is allowed to resume its former length, which it readily does if the operations are carried on in warm water, the first form of picture is again obtained, so that the effect is reversible. Silk does not possess any capacity for complete recovery after extension. Hair recovers completely after 30 per cent of extension ; beyond that there is only a partial recovery though it will stand an extension of 70 per cent before breaking.

Astbury has pointed out that these effects can be readily accounted for by supposing that the

\*Phil. Trans Roy Soc A Vol CCXXX, p 75, 1930

chain which forms the backbone of all the proteins is similar to that of silk. But in the keratins the chain is somewhat crumpled up. Tension pulls the chains straight without breaking them, so that the contractile forces, whatever they may be, can restore the chain to its old form, and the process of extension and contraction may be repeated indefinitely. Beyond the 30 per cent of elastic extension there is a possibility of further extension by means of the slipping of molecules past one another. This is practically the only form of extension possible in silk: it is not reversible.

A comparison of the two kinds of X-ray photographs supports this conception. The distance of repeat along the chain in stretched wool is only a very little less than that of silk, which is right if the stretching of the wool is due to the stretching of the chains, while the repeat in the unstretched hair is 30 per cent shorter than in the stretched. Other geometrical deductions from the photographs, some very definite, others less definite, are also in general agreement with the hypothesis.

But why should some keratin chains tend to crumple up while others do not? A plausible explanation can be readily given. The amino-acids and other pendants of the chain have a certain attraction for each other, at least if there are some which contain acid groups, while others have a basic character. All such attractions tend to shorten the chain. A rough model can be made to illustrate this point by stringing a number of wooden bars along a piece of flexible material as in Fig. 9. Elastic threads join the ends of the bars as shown and tend to draw them together.

The attractions simulated by the elastic links tend to shorten the chain, but an applied tension may break the connections so formed and give the chain its full length. This sort of thing cannot be expected to happen in the case of silk, because glycine and alanine have no attraction for each other, built as they are into the chain.

The same hypothesis gives a good explanation of the fact that hair and other keratin structures are so very resistant to chemical actions such as

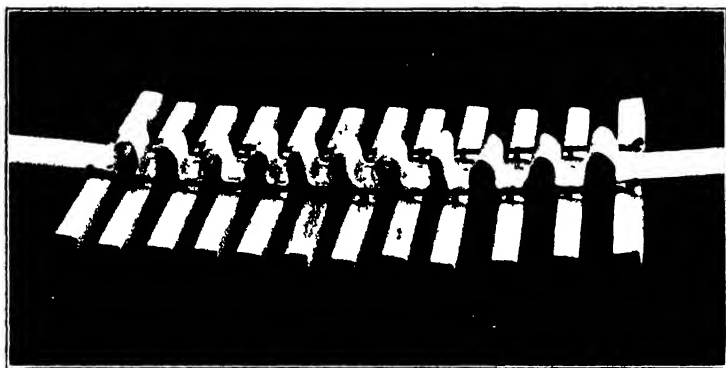


FIG 9

the attacks of enzymes. The crumpled chain protects itself in several ways. Its susceptible points are masked, partly by its compactness, partly by the previous satisfaction of tendencies to combination either in respect to groups belonging to the same chain or to different chains. Thus hair, horn and similar materials acquire a peculiar permanency often illustrated by the state of the remains in ancient tombs.

All these facts are illustrative of the statement with which I began, namely that not only does the arrangement of the atoms in the molecule decide the characteristics of the molecule but

also the arrangement of the molecules with respect to each other in the solid decides the behaviour of the solid. Arrangement of the protein molecules among themselves is essential to their function in the living body.

These general deductions regarding protein structure are only an earnest of what may be expected to follow from the precise measurements of position which we are now able to make. They are no more than indications of the directions in which knowledge of living structure may be able to advance as a consequence of the new methods of enquiry. Like any other new tool, X-ray analysis has to be in use for a certain time before its capacities are understood.

Besides the direct applications of X-rays which I have been describing there are certain other ways in which the substances of the living body have been studied by their aid. A most interesting example is the examination by J. D. Bernal and his colleagues of the crystal structure of the separate amino-acids, of the vitamins, and similar bodies. When such bodies can be crystallised valuable hints can be obtained as to the arrangement of the atoms and molecules, even if the structure cannot be fully determined. Chemical considerations suggest various possible arrangements, the choice from which may be narrowed down by the result of X-ray measurement. Thus, for example, Bernal showed that the formula proposed for sterol must be incorrect: in consequence a search for the proper formula was instituted and has seemingly been successful.

Bernal's investigations of the structure of these compounds are an example of one of the two

lines along which, broadly speaking, X-ray work is advancing. A series of like compounds is examined, and the various members are compared with each other. Information is derived from observations of the changes as the composition is varied step by step. In this particular research some twenty different substances have been compared. They are all members of a family of the greatest importance biologically. Their X-ray pictures show that they possess certain common characteristics of a structural nature, and the comparison of gradually changing quality with corresponding changes in certain dimensions, gives important hints as to constitution.

A new method often gives new force to older methods, and this is happening now. The optical, magnetic and other constants of a crystal show remarkable dependencies on the crystalline form. When we are able, as in this case, to determine the contents of the unit of pattern, and sometimes are able to go so far as to find the position of the atoms and molecules in the unit, the constants in question can be connected directly with the contents of the unit. Several years ago, W. L. Bragg showed how the refractive indices of calcite could be calculated in terms of the refractivities of the atoms and the arrangement in the calcite crystal which had just been discovered. So also, electrical displacement takes place with much greater ease in the plane of the aromatic benzene ring than normal to it. Consequently, the velocity, within the crystal, of light in which the vibrations are perpendicular to the ring is greater than light in which the vibrations lie in any other direction. This

principle can be used to help in the determination of the arrangement of the molecules in the crystal.

There is a second line of advance which is being followed; and the two modes of research support each other. In this other method the arrangement of the atoms in very simple crystals is worked out to the bitter end. The method is very laborious and cannot at present be applied to complicated cases. Molecules are chosen for investigation containing the atomic groupings which occur so widely, hydroxyl, carboxyl, benzene linkings and so on. Experiment shows, so far as it has gone, that the relative positions and orientations of the atoms in these common groupings are always the same or nearly so. If they are exactly determined from the examination of particular cases, the resulting rules can obviously be very helpful in the determination of structure, and also we may confidently hope, in the discovery of the *why* of a particular structure as well as the *how*.

On these lines several detailed investigations have been completed recently. One of the results has been a better understanding of the details of the linkages between carbon atoms. It is of especial interest in the study of organic compounds, and will serve as an illustration. It is well known that carbon linkages are not all the same; we speak of a single bond, a double bond and so on. According to the measurements we are now able to make, there are at least two kinds of carbon linkage differing primarily in the closeness of approach. There is the diamond linkage in which each carbon atom is at a distance of 1.54 Angstrom Units from its four

neighbours : and the graphite linkage where the distance is 1.42 between each atom and its three close neighbours. The difference between these is far greater than can be put down to experimental error. The former kind occurs also in the fatty acid chains, where each carbon also has four neighbours, two carbons and two hydrogens. The latter is found in anthracene and naphthalene, the basis of these substances being the benzene ring: in these the carbon has three neighbours as in graphite. It may prove to be the case that the former kind of bond is peculiar to the aromatic substances and the latter to the aliphatic. The heats of combustion of diamond and graphite are very nearly the same : so that it takes as much energy to break down the four bonds in the diamond as the three in the graphite. In such a comparison the heat spent on breaking the weak bonds between the net work layers of graphite is taken to be negligible.

Such accurate measurements as these encourage the hope that there are exact rules as to distances apart of the atoms, and very probably as to their mutual orientation. Knowledge of these rules will greatly facilitate the determination of structure.

What has been said above may serve to show how eagerly the new powers of detecting molecular arrangement in the solid are being used. With the knowledge gained in this way we may learn more of the forces which bind all atoms and molecules together, and in particular consolidate and give form and function to the various constituents of the living body.

[W. H. B.]



Friday, February 24, 1933

SIR ROBERT ROBERTSON, K.B.E., M.A., F.R.S.  
*Treasurer and Vice-President, in the Chair*

W. A. BONE, D.Sc., Ph.D., F.R.S., M.R.I.  
*Professor of Chemical Technology in the Imperial  
College of Science and Technology*

## THE PHOTOGRAPHIC ANALYSIS OF EXPLOSION FLAMES

### INTRODUCTION

ALTHOUGH the unaided eye familiarises us with stationary or slow moving flames it fails us completely when their speeds exceed a few metres per second, and it becomes necessary to resort to photographic analysis which nowadays is capable of such great accuracy and refinement that it is an indispensable part of the scientific study of explosions.

Let us consider a moment what flames are and why they move. Sir Humphry Davy taught us to regard them as "*aeriform or gaseous matter heated to such a degree as to be luminous,*" and the flames of combustible bodies as being in all cases "*the combustion of an explosive mixture of inflammable gas or vapour and air*" thus implying the continuous burning of an explosive mixture. And, for our purpose, his definition could hardly be improved upon.

When such a gaseous explosive medium is homogeneous and stationary, the flame moves through it at some definite velocity determined by a variety of circumstances, each successive burning layer of gas igniting the next one, either by "conduction" or by adiabatic compression, so that the flame-progress is continuous so long as any of the explosive medium remains unburnt. If, however, as in the familiar Bunsen flame, the explosive mixture itself is moving at the same speed as ignition is travelling in the opposite direction, a flame may appear stationary, though in truth its movement is merely balanced by an equal and opposite one. Such an apparently stationary flame is, therefore, no exception to the general rule that flames move in explosive media.

The velocities with which they move vary with circumstances, for example, such as the composition, temperature and density of the explosive medium, as well as the phase of the explosion; for in any medium an explosion begins relatively mildly but gathers force and velocity as it develops.

It should, however, be understood that by no means every mixture of a particular inflammable gas or air (oxygen) is explosive. Thus, for example, of hydrogen-air mixtures only those containing between about 4 and 75 per cent of hydrogen are explosive at room temperature and pressure, while for methane-air mixtures the range of inflammability is much narrower, being restricted to mixtures containing between about 5.35 and 14.85 per cent of the combustible gas. Indeed each inflammable gas has its own particular "range of inflammability" with air, and another and wider range with oxygen; moreover, each such range is widened at both ends by rise

in temperature, and in most cases at the upper end (or "limit") by increase in pressure. Another point to remember is that the nearer any given gas-air mixture is to one of the two limits of inflammability, the more slowly does it propagate flame in given circumstances; indeed what are called "speed-composition curves," in which initial flame speeds are plotted (ordinates) against mixture compositions (abscissae), assume the forms shown in Fig. 1, for a number of different gas-air media.

Although Sir Humphry Davy, in those classic researches which led up to his invention of the miner's safety lamp in 1815, was the first to elucidate the principles of flame propagation, it was not until Mallard and Le Chatelier applied photography to the problem fifty years ago\* that the successive phases of gaseous explosions were revealed and explored. And the method employed today for the purpose is in principle the same as that originally devised by them, namely photographing on a plate or film, moving vertically with known constant velocity, the movement of the flame along a horizontal tube. The chief difference between their procedure and ours is that, whereas they focussed the flame by means of a wide aperture lens, on a plate moving vertically at a constant velocity of 1 metre per second only, nowadays highly-sensitive films are moved vertically at any constant speed, up to about 200 metres per second, that may be most suitable for measuring the flame-speeds involved.

In all cases, however, the flame itself makes a photographic record compounded of its own horizontal velocity ( $V_1$ ) along the tube and that of

\* *Annales des Mines*, 8 Sér. IV, 1883. Pp. 274-318.

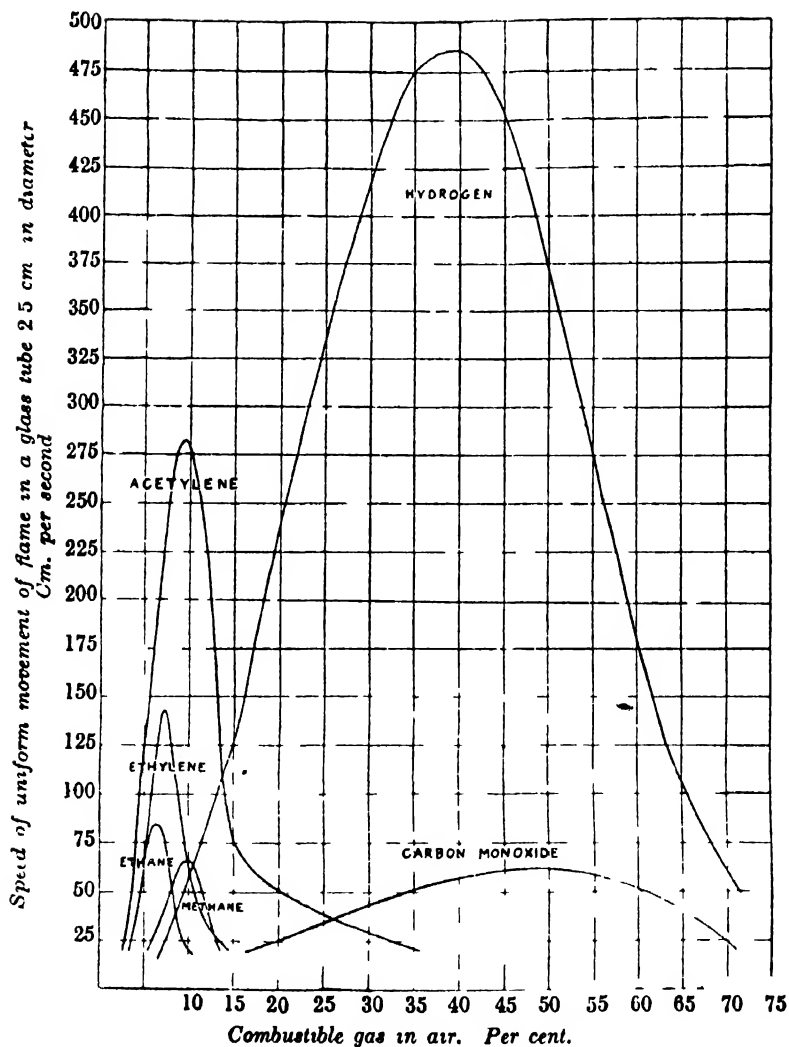


FIG 1

From "Flame and Combustion in Gases,"  
by Bone & Townend - By kind permission  
of Messrs Longmans, Green & Co., Ltd

the known vertical velocity ( $V_2$ ) of the film, from which not only may the flame movement be analysed but (provided the optical ratio between the tube and its image on the film be also known) its speed at any particular moment be calculated.

#### FORMER RESEARCHES 1883-1903

The plates available fifty years ago when Mallard and Le Chatelier began to photograph flames were not sensitive enough except for those of high actinic power ; so they confined their efforts to mixtures of carbon disulphide with either nitric oxide or oxygen, respectively, which they considered as representative of explosive mixtures generally with air or oxygen.

One of their first discoveries was that when an explosive mixture is inflamed in a tube, the initial flame movements differ according as ignition is effected near (*a*) the *open* or (*b*) the *closed* end. In the former case the flame always started and proceeded for a certain distance at a practically uniform slow velocity, which was then regarded as the true rate of propagation "by conduction," but is really materially less because of the hot products of combustion escaping from the open end of the tube. 'This initial "uniform movement" (as it was called) was generally succeeded by an "oscillatory period," the flame swinging backward and forward with increasing amplitude and finally *either* dying out *or* giving rise to "detonation" (or some similarly violent phase) according to circumstances. In true "detonation," which was first discovered by Berthelot and Vieille in 1881, the flame is propagated from layer to layer of the medium by adiabatic compression as a wave—sometimes called the "explosion wave"

—at a very high uniform velocity usually between about a mile or two per second. In some cases (e.g. certain “oxygen” mixtures) the initial period of uniform velocity was short and appeared to be succeeded abruptly by detonation without an intermediate “oscillatory” phase. When, however, ignition is effected near the *closed* end of the tube, the forward movement of the flame is usually continuously accelerated until finally detonation is (or may be) set up.

*Experiments.* Let us now make one or two experiments to verify some of these points.

Here is a horizontal glass tube 25ft. long by 2in. internal diameter, built up in sections and fitted at one end, which is open, with a device enabling it to be quickly filled “by displacement” with a coal-gas air mixture of any desired composition. Near the other end of the tube, which may be “open” or “closed” at will, are fitted firing wires for the ignition of the medium by an electric spark.

(1) First of all let us fill the tube with an explosive gas-air mixture of a composition approximating to that of the “lower limit” mixture, i.e. one containing just sufficient coal-gas to render it explosive. Now, on igniting it near the far end, which is kept *open*, we shall observe a bluish flame travelling slowly along the tube with an almost uniform slow velocity, characteristic of the initial phase of such an explosion.

(2) By the suitable re-adjustment of the filling device we will next increase the proportion of gas in the medium until its composition approximates to that of the most explosive coal-gas air mixture. On igniting it, (a) again near the open end, it will

be observed that the initial uniform flame-movement, which is now faster than it was in (1), is soon succeeded by an oscillatory phase; and on (b) repeating the experiment but with the end nearest the igniting spark *closed* instead of open, we shall see that the flame-movement is much faster and exhibits neither any initial uniform movement nor oscillatory period, but is continuously accelerated from the beginning.

(3) By once more re-adjusting the filling device we will again increase the proportion of gas in the mixture until its composition is near that of the "upper limit" of inflammability. On again igniting it near the *open* end, we shall observe a similar effect to (1) save that now the flame, instead of being homogeneous, has a bluish head and a lilac coloured tail.

(4) To demonstrate further the development of an explosion, we will next ignite a  $\text{CS}_2 : 6\text{NO}$  medium at the upper and *open* end of a vertical glass tube, some 6ft. long and 2in. diameter the lower end of which is closed. Observe the brilliance of the flame and that an initial mild "uniform" movement is soon succeeded by a noisy "oscillatory" one; indeed, were the tube much longer, "detonation" would be set up with "shattering" effect.

(5) In order to satisfy ourselves of the characteristic violence and instantaneousness of the final phase of "detonation" in such gaseous explosions, a moist  $2\text{CO} + \text{O}_2$  mixture will now be fired in a leaden coil (10ft. long by 0.5 in. diameter) to the firing end of which is fitted a closed "detonation-box" i.e. a device for setting up "detonation" almost instantaneously, the other end terminating in a closed glass tube. A deafening

report will immediately be heard, and the glass tube will be pulverised by the force of the explosion, the whole happening within so short a time that we are quite insensible of its duration, although actually it would be something of the order of  $1/100$  second.

The function of the detonation-box, with its labyrinth of narrow zig-zagged passages was to generate a rapid succession of compression waves which impinging on the nascent flame rapidly accelerated it to the speed of "detonation." To demonstrate this we have connected such a box in series with a Teclu atmospheric burner; on turning it on and passing a spark near the exit from the box a deafening report will be heard. Indeed, as will become more evident later, during the earlier phases of a gaseous explosion, combustion is relatively slow and only part of it occurs in the flame front itself, the remainder occurring behind it, so that the flame always has appreciable volume. And the rapidity of combustion in the flame depends largely on the accelerating influence of compression waves traversing it.

Excellent examples of the analysing powers of the cameras available more than thirty years ago are afforded by a beautiful series of seventy or more photographs of explosion flames published in a memoir by the late Professor H. B. Dixon in 1903.\* He used a sensitive Eastman film fixed on the periphery of a light metal drum 1 metre in circumference rotated in a vertical plane by means of a motor provided with gearings so as to produce at will constant vertical film-speeds of 25, 50 or 100 metres per second, the last-named corresponding with 6,000 revolutions of the wheel per minute.

\* *Phil Trans Roy Soc*, A 200, 1903, pp 315-352



Usually a film-speed of either 25 or 50 metres per second was employed, the length of the explosion tube actually photographed being thirty times that of its image when focussed on the film ; and with such apparatus he photographed phenomena associated with the successive stages in the development of explosions in various gaseous media, but mainly in mixtures of cyanogen and oxygen.

Unfortunately time does not permit of my showing more than three of the resulting photographs. The first (Pl. 16, Fig. 55 in the memoir, *loc. cit.*) shows the development up to detonation of an explosion in a  $\text{CS}_2 + 5\text{O}_2$  medium initiated by a spark about 4 inches away from the closed end of a long horizontal tube the far end of which was also closed ; the second (*ibid.*, Pl. 11, Fig. 17) shows the subsequent detonation wave dashing through the medium, noticeable features being the brilliance of the flame-front and the movements of the medium en masse as it follows up the detonation wave, and swings back again ; while the third (*ibid.*, Pl. 18, Fig. 68) is of the oscillatory period when the medium was fired near the *open* end of a tube.

From the researches of Mallard and Le Chatelier in France, and of H. B. Dixon in this country during the years 1883 to 1903 we learnt not only to distinguish at least three phases in the development of a gaseous explosion, but also the influence of compression waves thereon, and the throwing-back of a strong "retonation" wave through the still burning gases behind the flame-front at the moment when "detonation" is set up, such "retonation" traversing the incandescent medium at a speed but little inferior to that of "detonation" itself and making a highly luminous track there-through.

RECENT DEVELOPMENTS AT THE IMPERIAL COLLEGE,  
SOUTH KENSINGTON

## THE FRASER HIGH-SPEED CAMERAS

In 1925 our research staff at the Imperial College was joined by Mr. R. P. Fraser, and on finding that his bent was high-speed photography I set him to work on further developing the old experimental method with a view to increasing its analysing power more particularly for the exploration of "detonation," which demands much more rapid film movements than any formerly employed. To meet the heavy expenses involved we have been indebted at various times to the generosity of Radiation, Ltd., Messrs. Nobel's Explosives Company, Ltd., and Imperial Chemical Industries, Ltd., and latterly to a grant from the Messel Fund of the Royal Society in whose Proceedings and Philosophical Transactions our principal results have been published.\*

Time does not permit of my describing the wonderful new high-speed cameras which Mr. Fraser has designed and had constructed for the work, and whose accuracy and analysing powers have far surpassed anything yet achieved. Suffice to say that first of all he set out to improve and develop the old revolving-drum method until in 1928 a 9-inch duraluminum drum could be rotated within the camera at any desired constant speed up to 16,000 r.p.m., or equivalent to any constant film speed up to nearly 200 metres per second, at which it became possible for the first time to photograph and measure with considerable accuracy periodic movements in explosion flames with frequencies up to 250,000 per second. There is

\* Chiefly in *Phil Trans*, A 228 (1929), pp. 197-234, and A 230 (1931), pp. 363-84.

no great difficulty, provided one knows how, in maintaining the film intact on the drum at such high speed, but beyond it the safety limit in rotating such a drum is approached. Not long before his death, after he had spent a day with us studying these new possibilities, the late H. B. Dixon wrote saying how he "envied us the luxury of our feelings" in the possession of so powerful a weapon.\*

Not content with such notable achievement, however, Mr. Fraser next designed in 1931 our latest camera in which an 8-lbs. stainless steel mirror is revolved *in vacuo* at any desired constant speed of up to 30,000 r.p.m. and projects the image of the explosion flame on to a stationary film. The analysing power of this new camera, which has been successfully working a year now, is four or five times greater than that of its immediate predecessor, and will enable us to measure with precision periodic flame movements occurring with frequencies up to a million per second. It is indeed a wonderful instrument, which later may be applied to the study of detonation in solid explosives, and our only regret is that Dixon did not live to see it.

### SOME NEW PHOTOGRAPHS OF EXPLOSION FLAMES

A selection of our flame-photographs obtained by means of these cameras is exhibited in the Library, and a few of the more interesting will now be shown on the screen and their principal features pointed out.† Please remember that the vertical

\* *Nature*, 124 (1929), p. 580.

† As only some of these are reproduced herein, in other cases references are given to the original plates in *Proc.* or *Phil. Trans. Royal Soc. A* (*loc. cit.*), where they may be found, the numbers in heavy type indicating the particular volume concerned.

direction in them represents time (sometimes a time scale in milliseconds being attached) and the horizontal direction the length of the explosion tube photographed.

## FIRST SERIES RELATING TO THE INITIAL AND PRE-DETONATION PHASES



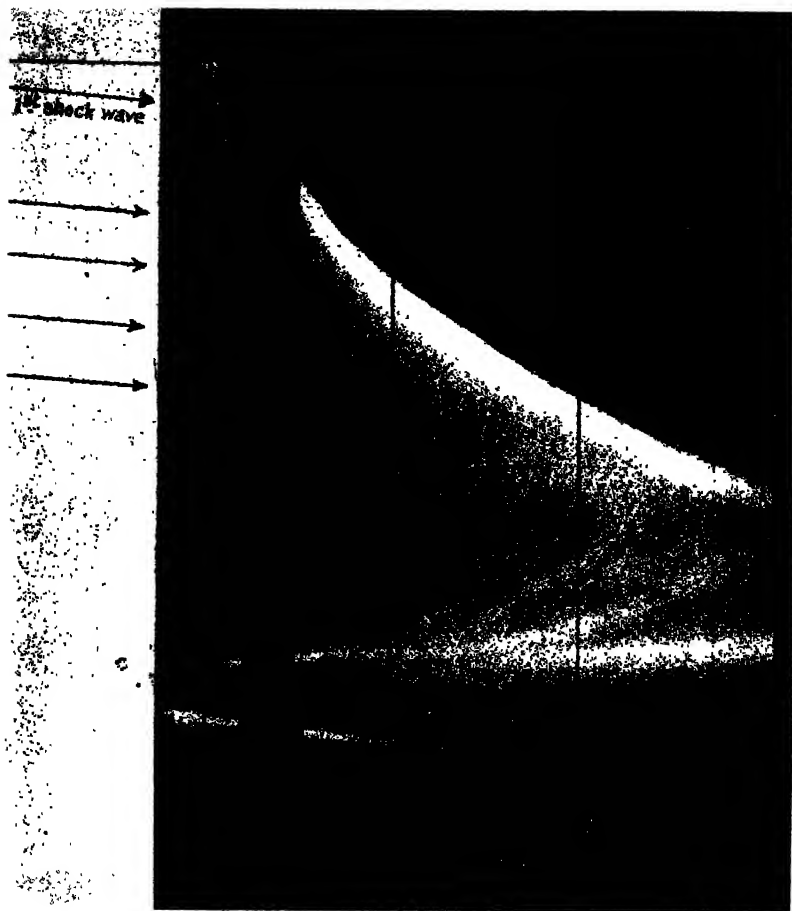
No. 1.

(1) *Of a  $CH_4 + O_2$  Explosion.* The first is a beautiful photograph showing the development of an explosion in an equimolecular methane-oxygen mixture ( $CH_4 + O_2$ ) which was ignited by a powerful condenser discharge between platinum electrodes situated midway along a horizontal glass tube 35 cms long and 2 cms internal diameter closed at both ends. The photograph (No. 1 and Proc. Roy. Soc.

A 114 Pl. 33, No. 3) enables us minutely to analyse the course of events. It will be seen that immediately on the discharge a feebly luminous flame was propagated fairly symmetrically, with at first continuously accelerated velocity for a

distance of nearly 10 cms towards each end of the tube. There then ensued a marked deceleration of the velocity which soon became and continued nearly uniform until each flame-front had nearly reached the end of the tube. Meanwhile, highly luminous *striae*, suggestive of streams of activated gases, originated in each flame front, and passing backwards through the still-burning medium they converged and finally coalesced not far from the middle of the tube; whereupon a sudden outburst of intense luminosity occurred, the whole medium instantly becoming brilliantly incandescent and traversed by compression waves. Another notable feature is the evidence of incandescent metal particles being shot from the electrodes in straight tracks through the medium but without affecting the intensity of the combustion. The duration of the initial phase of relatively feeble general luminosity was about 4 milliseconds only, and that of the final phase of intense luminosity another 4 milliseconds so that the whole series of events here portrayed happened well within 1/100 second which, however short as it may appear to us, is quite a long time as explosions go.

(2) *Of a Compression Wave Traversing the Burning Medium.* An excellent example of such traversing of the medium by compression waves during the second phase of an explosion is given in the next photograph (similar to Phil. Trans. A 228, Pl. 8, No. 33) which is of the phenomenon in a  $2\text{CO} + \text{O}_2 + 2\text{H}_2$  explosion in a closed tube 35 cms long and 2 cms internal diameter. Two compression waves are seen criss-crossing in the still burning medium behind the flame-front, their velocities being about 1,000 metres per second.



No 2.

(3) *Of the Influence of Extraneous Shock Waves.*

Although such compression waves arise autogenously within the flame during explosions in closed tubes, by suitable means they may be generated extraneously and imposed upon an advancing flame, causing abrupt accelerations of its speed until detonation is set up. Such shock waves travel through the medium with a velocity equal to, or, if they are intense enough, even greater than, that of sound ; and it is convenient to distinguish between two conditions according as the flame is advancing with a velocity less or greater than that of any shock wave which may either be following it or have passed through it. For an advancing flame may be overtaken by, or be overtaking, shock waves according to its velocity in relation to theirs. And for convenience we may call the first condition the "initial" and the second the "pre-detonation" phase of an explosion.

(a) The next photograph (No. 2 and Phil. Trans. A 228, Pl. 9, No. 35) shows an explosion flame in a  $2\text{CO} + \text{O}_2$  medium being overtaken, during the initial phase, by a succession of such shock waves at intervals of  $1/400$  second. The distance actually traversed by the flame in the photograph from the point of ignition is 0.65 metre during which it was overtaken by five successive "shock waves" each of which abruptly accelerated its speed ; hence six successive uniform flame-speeds are shown, the first being very small, and the others 9.2, 71.5, 76.4, 101.1 and 122 metres per second respectively. These shock waves, having passed through the flame, travelled on ahead of it ; but it is obvious that, with further repetition of them, the flame speed would soon become greater than theirs, in which case the

position would be reversed, so that the flame, instead of being overtaken by the following shock wave, would now begin to catch up with and overtake those which had previously passed through it. (b) This new condition (the "pre-detonation phase") is illustrated in the next photograph (No. 3 and Phil. Trans. A 228, Pl. 15, No. 10)



No 3

which shows the accelerated flame during the third metre run of a  $2\text{CO} + \text{O}_2$  explosion overtaking two successive "shock waves" ahead of it. As it enters the photographic field the flame is already travelling at a speed of 900 metres per second, but shortly afterwards it catches up with the rearmost of the two shock waves. This causes a new ignition about 3 inches (7.3 cms) ahead of the



flame and the new flame thus initiated starts off with a velocity of 1,460 metres per second, a "retonation wave" being simultaneously sent back through the medium with a velocity of 855 metres per second. About 1/3000 second later, the flame catches up the second "shock wave" causing another ignition about 1.5 inches (3.4 cms) ahead of it. This second ignition ahead sets up "detonation" with a constant velocity of 1,940 metres per second\*, and simultaneously a "retonation wave" is thrown back with a velocity of 980 metres per second through the still burning medium behind the flame front.

## SECOND SERIES RELATING TO THE PHENOMENON OF "SPIN" IN DETONATION

In detonation, which is the final and most intensive phase of a gaseous explosion, the flame is propagated from layer to layer through the medium by adiabatic compression at a very high speed, which is constant for each particular medium under given physical conditions, but varies between one and two miles per second according to the composition of the medium. Berthelot and Vieille, who discovered the phenomenon in the year 1881 and called it "*l'onde explosive*" ("the explosion wave"), likened it to a sound wave passing through the medium with the difference that whereas a sound wave is propagated from layer to layer with a small compression, in the explosion wave, there is propagated an abrupt change in chemical condition which generates an

\* In cases, such as this, where detonation is set up under the influence of very strong extraneous "shock waves," its velocity may be higher than when set up autogenously; the *normal* velocity for a  $2\text{CO} + \text{O}_2$  medium is 1760 metres per sec.

enormous force as it passes through each successive layer of the medium. About twenty years later this sound wave theory was modified by Vieille in that he now regarded it as a special type of "shock wave" in which an abrupt change of pressure in the vicinity of the wave front is maintained by the adiabatic combustion of the medium through which it is propagated.

Since its discovery, it has been generally considered that in the explosion-wave chemical change is propagated under the most intensive conditions of temperature and pressure, and therefore with the utmost rapidity; and it seems probable that practically all collisions between the molecules of oxygen and combustible in the flame-front must be fruitful of change, and accordingly the flame is highly luminous and of extremely short duration, probably not exceeding at the most  $1/1000$  second.

From the earlier investigations upon detonation of Berthelot and Vieille, and Mallard and of Le Chatelier in France, as well as of H. B. Dixon in this country, it was concluded that the wave-front is homogeneous as regards temperature, pressure and chemical action. This view prevailed until the year 1926, when Dr. Colin Campbell and Mr. D. W. Woodhead in photographing certain detonation flames discovered – what we afterwards also observed independently – that they are not homogeneous, but exhibit a highly luminous comet-like "head" of detonation with a long luminous "tail" rotating with a frequency (according to the nature of the medium and the diameter of the tube) of several tens of thousands a second. This "head" of detonation passes down the tube along a spiral track close to the walls,

producing in the flame-photograph the appearance of a sinuous (instead of a straight) wave-front together with a banded appearance of the flame behind it, and the phenomenon is now referred to as that of "spin" in detonation. And, according to our experience so far, the spiralling is usually clock-wise, though not invariably so.

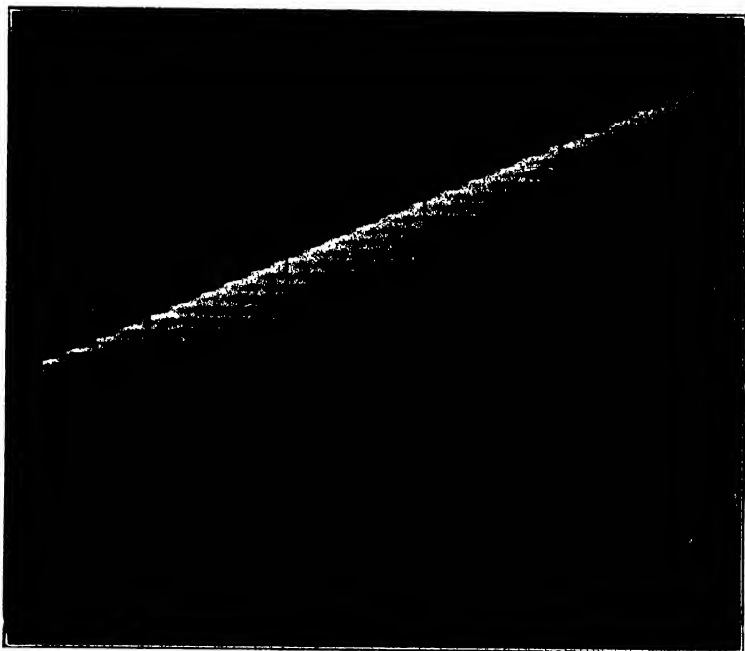
Since 1927 we have been employing the high analysing powers of our cameras for its exploration, and although as yet our task is by no means finished, we have already discovered certain features in it of outstanding interest which I will now endeavour to set forth. It should, however, be understood that whereas the photographs of detonations in many explosive gaseous media give evidence of "spin," there are some (e.g. those in hydrogen and oxygen mixtures) which as yet have not done so, although it seems possible that in such cases either the "spin" is of such a frequency, or there are so many "heads" of detonation involved, that even the analysing powers of our camera have not yet been able to detect them.

As the phenomenon is exemplified most beautifully by detonations in carbonic oxide-oxygen media, I will deal mainly with such cases, although others may be mentioned incidentally.

(1) *Of "Spin" in a  $2\text{CO} + \text{O}_2$  Detonation.* This photograph (No. 4, similar to Phil. Trans. A 228, Pl. 11, No. 39 reproduced here) shows the phenomenon in the detonation of a  $2\text{CO} + \text{O}_2$  medium in a tube of 0.5 inch (1.25 cms) internal diameter. Here the frequency was 44,000 per second, and the forward velocity of the flame 1750 metres per second, the time taken in traversing the distance shown was about  $1/2000$  second, and the total

duration of luminosity behind the flame-front rather more than  $1/1000$  second.

(2) *Of a Self-Recorded Helical Track of "Spin" in a  $2\text{CO} + \text{O}_2$  Detonation.* That the phenomenon is really due to a material "head" of detonation spiralling down the tube along a helical track has



No. 4.

been conclusively shown in explosions in which the glass section of the explosion tube actually photographed was inserted between two long lengths of lead tubing of the same internal diameter. In such cases, a preliminary explosion suffices to deposit on the inner surface of the glass section a thin grey film of lead ; and in subsequent experiments the intensively luminous head

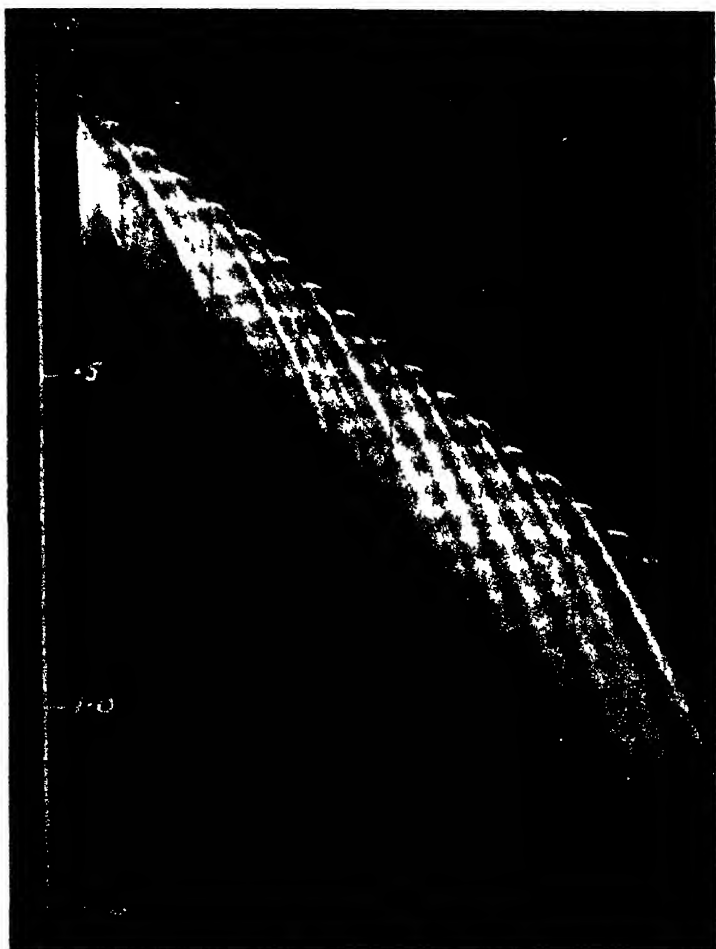
spiralling along it volatilises the lead particles in its path, and thus records its own track. The next photograph (Phil. Trans. A 228, Pl. II, No. 40) shows such a self-recorded track in a  $2\text{CO} + \text{O}_2$  detonation along a glass tube of 0.5 in. internal diameter, the frequency being about 49,000 per second. The tube itself, with the spiral track on it, is here on the table for your inspection. The experiment has been repeated using a glass tube on the inner wall of which a thin mirror of silver was chemically deposited; and, as can be seen on inspecting it, the spiralling head of detonation cut out its track along it.

(3) *Of the Persistence of "Spin" in a  $3\text{CO} + \text{O}_2$  Detonation.* Once established, the spin persists indefinitely so long as there is no interruption of conditions or obstruction in the tube. This is well shown by the next photograph (Proc. Roy. Soc., A 130, Pl. 8) of a moist  $3\text{CO}_2 + \text{O}_2$  detonation in which the lead coil had two 1.5 metres horizontal glass sections, 60 metres apart, but arranged parallel-wise one above the other so that the flame traversed the lower one in one direction and afterwards the upper one in the reverse direction, both being photographed on the same film rotating with a vertical speed of 87.85 metres per second. It will be seen that the resulting flame-photographs are perfectly symmetrical. Both subtend exactly the same angle ( $49.5^\circ$ ) with the vertical, corresponding with flame speeds of 1,775 metres per second in each case, and the frequency of the "spin" is the same in both, namely 44,400 per second.

(4) *Of "Spin" in a  $2\text{CO} + \text{O}_2$  Detonation.* The next photograph (No. 5 and Phil. Trans. A 230, Pl. 16, No. 14), one of the best so far obtained, is

of a  $2\text{CO} + \text{O}_2$  detonation in a tube of an inch (2.5 cms) diameter. Here the spin frequency was 24,000 per second and its pitch 7.5 cms, while the forward velocity of the flame-wave as a whole was 1,795 metres per second, the medium itself following it at a speed of 1,175 metres per second. The duration of the events recorded in this case was about 1 1000 second, the banded appearance and luminosity behind the flame front being limited by the shattering of the tube by the force of the explosion. This, however, did not prevent the flame being perfectly photographed.

(5) *The Influence of Tube-Diameter upon the "Spin" — Multiple "Heads" of Detonation.* It should here be observed that although it was formerly believed that in detonation the flame-speed for a particular medium under given conditions of pressure and temperature is independent of the diameter of the tube, from these photographic researches we now know that, wherever "spin" is developed, this is not strictly so. Both Campbell and Woodhead and ourselves have found that in a  $2\text{CO} + \text{O}_2$  detonation, where (up to tube diameter of 1 inch) there is only *one* spinning "head" of detonation, the ratio of the pitch of the "spin" to the tube diameter is always very nearly 3.0 and the velocity of the rotating head along its helical path nearly constant at between 2,500 and 2,600 metres per second. When, however, the tube diameter exceeds one inch or thereabouts, two or more spiralling "heads" of detonation may be developed, in which case the said ratio is not maintained, the photograph (Phil. Trans. A 230, Pl. 17, No. 21) having a rather confused appearance owing to the two heads



No. 5.

rotating in and out of phase (pitch = 4.5 and 9.35 cms instead of the calculated 12.15 cms for a single head).

Moreover, in a  $\text{CH}_4 + \text{O}_2$  detonation, in a tube of 0.5 inch internal diameter, we have observed three distinct rotation-frequencies of 68,000, 110,000 and 227,000 per second respectively, the first of which was developed just before detonation was established and the second immediately afterwards, the pitch being nearly the same in both. The third apparent frequency of 227,000 per second was due to two heads of detonation each rotating at the second frequency.

(6) *The "Spin" not due to Rotation of the Medium itself.* When first discovered, it was suggested that the "spin" observed in detonation involves the rotation of the gaseous medium as a whole; but such is hardly credible inasmuch as (say) in the case of a  $2\text{CO} + \text{O}_2$  detonation in a tube of 0.5 inch internal diameter it would mean that the whole mass of the medium, both in the flame-front and for something like a metre behind it, would be rotating with a peripheral speed of about 2,000 metres per second. The matter was definitely settled by photographing detonations of a  $2\text{CO} + \text{O}_2$  mixture in (a) a glass tube of 1.3 cms internal diameter having along its whole length a longitudinal "ridge" projecting 1 mm into the medium and (b) a glass tube of same diameter but without any such ridge. For, had the "spin" involved any such rotation of the medium as a whole, the "ridge" in the first case would assuredly have upset it altogether; but the photograph proved that in fact it had no effect whatsoever on the course of events, as the following figures show:



$2\text{CO} + \text{O}_2$  DETONATIONS IN A TUBE OF 1.3 CM INTERNAL DIAMETER

" Characteristics of Spin "			Pitch cms.	Velocity of Flame Front. metres per sec.
		Frequency per sec.		
(a) With Ridge	...	44,000	3.95	1,750
(b) Without Ridge	...	44,000	3.95	1,780

Hence, whatever explanation of the phenomena may finally be forthcoming, any idea of rotation of the medium as a whole must be ruled out. It would seem more probably to depend on the establishment of a condition something like that of a "stationary wave" in the medium. My colleague, Prof. H. Levy, who is considering the mathematical aspects of the matter, has suggested that the combustion in the flame, involving as it does rapid evolution of heat, entails the passage of a rapid agitation of molecules through the gaseous medium, corresponding very closely with the head of a wave. Presumably such a "wave" would change shape in passing along a tube with accelerated velocity, and quite possibly it might give rise to a spiral wave front when a certain high speed is exceeded; and, if so, combustion would continue to travel along a special path at a speed corresponding with the wave speed of the combustion in the flame-front, in which case the medium would not move spirally as a whole, but a wave front would travel spirally through it.

(7) *Of the Effects of a Strong Electric Field upon the Head of Detonation.* The association of the "spin" with an intensely luminous "head" of detonation suggests the latter being a localised concentration of highly excited, and possibly

completely ionised, particles in a state of extreme chemical activity. And if so, the phenomenon would presumably be affected on entering a sufficiently strong electric field, and on putting the matter to an experimental test it has proved to be so.

In these experiments photographs were taken of a series of  $2\text{CO} + \text{O}_2$  detonations in a tube of 0.5 inch internal diameter fitted with a glass section in which a strong electric field could be maintained between two electrodes—one of which was a ring-shaped silver mirror specially deposited on the inside of the tube—separated by a distance of 30 cms.

In a blank experiment (a) with no field, the flame passed through the glass section with a constant velocity of 1,755 metres per second showing a quite normal "spin." And on (b) the flame entering and crossing a field of 80,000 volts in the + to — direction, the "spin" was unimpaired, although the forward velocity of the flame fell to 1,720 in crossing, but rose again to 1,770 metres per second on leaving the field, thus being slightly retarded between the electrodes. But (c) on reversing the polarity of the field, so that the flame entered by its — boundary and crossed it from — to +, not only was the spin quickly and entirely suppressed, but "detonation" ceased and the flame speed was rapidly reduced from 1,755 to 910 metres per second.

Such experiments indicate that the "head" of detonation is a positively charged region, and that so soon as the positively charged particles (whatever they may be) in it are either neutralized or removed, the detonation ceases.

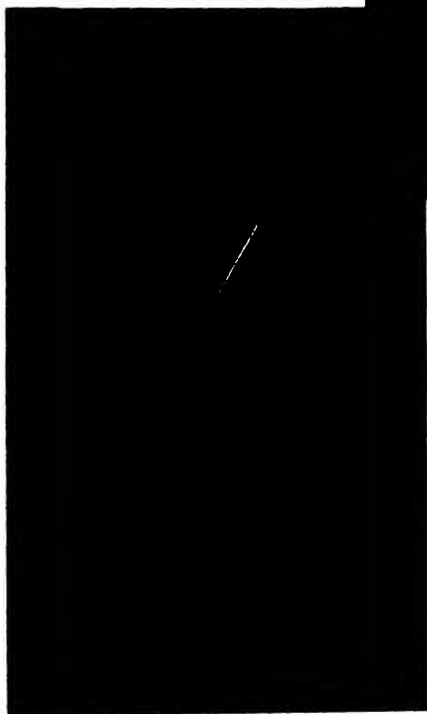
(8) *Of the "Banded" Appearance of the Flame*

*behind the "Head" of Detonation.* The peculiar "banded" appearance of the flame behind the "head" of detonation was at one time attributed to a long luminous "tail" lying close to the wall of the tube, and rotating with a frequency almost identical with that of the "head" of detonation, but slightly diminishing as the distance therefrom increases. When, however, we were able to invoke the greater analysing power of our latest camera, it was soon seen to be an optical effect arising from the mutual criss-crossing of two other phenomena originating in the "head" of detonation. Although rather difficult to bring out clearly in a lantern slide, they can be seen very well in a photographic enlargement taken direct from the original negative of a  $2\text{CO} + \text{O}_2$  detonation in a tube of 0.5 inch internal diameter, the part photographed representing the course of events during  $1/8000$  second only. It will be seen that the luminosity of sinuous tracks of the head of detonation varies intermittently in a manner suggestive of a series of rapidly alternating intensities of chemical action. And at each successive increase in luminosity there originate simultaneously (i) a luminous stream travelling forward with a velocity less than that of the flame-front and (ii) what appears to be a compression wave thrown backwards through the burning medium. And the nearly horizontal "bands" are now seen to be resolved into a series of enhanced illuminations of the medium at the criss-crossing of the two effects referred to.

(9) *Of a Detonation in Acetylene.* As a concluding illustration of the insight into detonation-flames given by our high-speed camera let me direct attention to two remarkable photographs of a



No 6



No 7

detonation in pure acetylene. This gas ( $C_2H_2$ ) being, as many of you know, strongly endothermic—its molecular heat of formation being  $-47.8$  K.C.U.'s—its molecules are unstable and under the influence of "shock" waves readily decompose into their elements carbon and hydrogen with such liberation of energy that, when the gas is under pressure, the decomposition is propagated from layer to layer indefinitely as a "detonation," exemplifying a single gas behaving as a high explosive. At atmospheric pressure, even, it may be caused to "detonate" under the influence of a sufficiently strong shock wave; but in such circumstances the detonation is apt to die out after proceeding a certain distance owing to the energy of the shock wave concerned gradually being dissipated, although the latter may continue for a while thereafter. The two photographs (Nos. 6 and 7 and Phil. Trans. A **230**, Pl. 19, Nos. 28 and 29) relate to an experiment in which pure acetylene was caused to "detonate" at atmospheric pressure in a long glass tube of 1.4 cms internal diameter by the imposition of a strong "shock" wave from an external source. The first photograph (No. 6) shows the actual "detonation" during its first metre run. Here the imposed shock wave causing the detonation accompanies it, their joint propagation being marked by a an intensely brilliant flame, propagated with a velocity of 2,160 metres (i.e. about  $1\frac{1}{3}$  miles) per second, and an instant resolution of the gas into carbon and hydrogen. A well-marked "spin" (pitch = 5.69 cms, and frequency = 38,000 per second) was developed after a 40 cms run and continued, with diminishing frequency, until the flame speed had fallen to about 1,470 metres per

second. The total duration of the events recorded in the photograph being just 0.66 millisecond.

The next photograph (No. 7) shows the course of events during the succeeding 1.75 milliseconds. The decomposition of the gas, although continuing, has now ceased being propagated as a "detonation"; the initiating shock-wave traverses the medium with decelerating velocity, raising the acetylene in its track to incandescence, but not (as formerly) causing it instantaneously to decompose. Its decomposition, as it were, lags behind the shock wave, there now being a short but steadily increasing dark interval between the incandescent flame-front and the luminous decomposition of the acetylene behind it. Thus the photograph enables us to discern first of all the gas being raised to brilliant incandescence in the track of the "shock" wave passing through it, then an extremely brief dark interval, increasing from  $1/20,000$  to  $1/5,000$  second, during which the vibrating molecules elude the dissolution which finally overtakes them, and which is evidenced by the separation of luminous carbon particles causing a "feathery" appearance behind the track of the wave itself.

[W. A. B.]

*Photographs Nos. 1 to 7 reproduced by  
kind permission of the Royal Society.*

Friday, March 10, 1933

SIR ROBERT ROBERTSON, K.B.E., M.A., F.R.S.  
*Treasurer and Vice-President, in the Chair*

THE LORD RUTHERFORD OF NELSON,  
O.M., F.R.S., M.R.I.  
*Professor of Natural Philosophy*

RECENT RESEARCHES ON  
TRANSMUTATION OF THE ELEMENTS

[ABSTRACT].

IT is now well established that the change of one atom into another can only be effected by the addition or subtraction of one of the constituent particles of the atomic nucleus, for example, an electron, proton, neutron or  $\alpha$ -particle. Such a transformation was first accomplished in 1919 for the element nitrogen by bombarding it with swift  $\alpha$ -particles from radio-active substances. About one  $\alpha$ -particle in 100,000 comes so close to the nucleus that it enters and is captured by it. This violent disturbance results in the expulsion of a proton with high speed, and the formation of a new nucleus of mass 17. A number of light elements can be transformed by  $\alpha$ -particle bombardment in a similar way, and in most cases a proton is ejected.

A new and strange type of transformation was discovered last year by Chadwick: when  $\alpha$ -particles bombard the metal beryllium, uncharged particles of mass 1, called neutrons, are expelled. These neutrons, which have remarkable powers of penetrating matter, are themselves very efficient agents for the transformation of atoms. Feather has shown that both nitrogen and oxygen are transformed by the capture of neutrons, with the expulsion of a fast  $\alpha$ -particle. The types of transformations produced by the neutron are thus very different from those observed with the  $\alpha$ -particle. The capture of an  $\alpha$ -particle in general leads to the building up of a new nucleus three units heavier than before, while the capture of a neutron leads to the formation of a nucleus three units lighter.

During the past year, Cockcroft and Walton in Cambridge made the important discovery that comparatively low speed protons are very effective in causing the transformation of a number of elements. The protons are generated in large numbers by an electric discharge through hydrogen, and then speeded up by passing through an evacuated space to which a high potential of the order of 600,000 volts is applied. Under these conditions the protons acquire a high speed comparable with that of the  $\alpha$ -particle from radium. When a stream of these swift protons falls on the element lithium, a large number of  $\alpha$ -particles are emitted of individual energy comparable with that of the swiftest  $\alpha$ -particle from radium. It seems that about one in 100 million of the protons enters a lithium nucleus of mass 7, and the resulting nucleus of mass 8 splits up into two  $\alpha$ -particles, each of mass 4. Cockcroft and Walton have later



found that the  $\alpha$ -particles emitted consist of two groups differing widely in speed.

This transformation of lithium can be produced at surprisingly low voltages. With strong proton streams, the emission of  $\alpha$ -particles can be observed for 30,000 volts; the number of particles increases rapidly with the voltage, and the variation has been examined by different observers over a very wide range, from 30,000 to  $1\frac{1}{2}$  million volts.

Protons are also remarkably effective in disintegrating the light element boron, and again  $\alpha$ -particles are emitted. It is possible in this case that the boron nucleus of mass 11, after capturing a proton, breaks up into three  $\alpha$ -particles. The radiation observed is complex, and has not yet been analysed in detail. A number of other elements have been found to be transformed, apparently in all cases with the emission of  $\alpha$ -particles.

An account was given of a special form of accelerating tube, devised by Oliphant in the Cavendish Laboratory, in which a narrow intense proton stream can be generated at voltages up to 200,000 volts. The protons, after being bent by a magnetic field, bombard a target of about one square centimetre in area. By special arrangements, it has been found possible to obtain in the detecting chamber at least 1,000 times the number of particles observed by Cockcroft and Walton at the same voltage. By this method it is possible to observe the  $\alpha$ -particles from thin films of lithium and boron at comparatively low voltages, while the variation of number with voltage has been measured. For example, a number of  $\alpha$ -particles are emitted from lithium as low as 30,000 volts.

$\alpha$ -Particles from boron have been observed at 60,000 volts, but the number increases much more rapidly with voltage than in the case of lithium.

Special experiments have been made to test by this sensitive method, whether the heavy elements thallium, lead, bismuth and uranium show any evidences of transformation for 200,000 volts protons, but no sign of increased emission of  $\alpha$ -particles has been observed for these elements. At first, marked effects were observed, but these were ultimately traced to a minute contamination by boron, probably originating in the discharge tube. It seems not unlikely that the effects observed for uranium and lead in the original experiments of Cockcroft and Walton may have been due to an unsuspected contamination by a minute trace of boron.

During the last few years much energy has been devoted throughout the world to developing methods of obtaining streams of very swift charged particles with which to bombard matter and effect its transmutation. In the apparatus of Cockcroft and Walton in Cambridge already referred to, a steady potential of 800,000 volts can be reached. A new and simple type of electrostatic generator has been designed by Van der Graaf and Atta in the Massachusetts Institute of Technology, with which they have obtained a steady potential of  $1\frac{1}{2}$  million volts, and a larger apparatus is under construction with which they hope to obtain a potential of 15 million volts to apply to a large vacuum tube. Brasch and Lange have applied high momentary voltages to a discharge tube by using an impulse generator.

A new and ingenious method of multiple acceleration has been devised by Lawrence of the

University of California with which he has already obtained protons of energy  $1\frac{1}{2}$  million volts by using a potential less than 10,000 volts. The transformation of lithium has been examined at this high energy using a proton current of about a thousandth of a micro-ampere. It is hoped to develop this method so as to obtain protons of energy as high as 10 million volts or more.

Even if these new projects prove successful, the speeds of particles produced by their aid are much smaller than those observed for the very penetrating radiation in our atmosphere, where electrons and protons of energy from 200 million to 2,000 million volts are present. From the experiments of Anderson in Pasadena and Blackett and Occhialini in Cambridge, it seems certain that these very swift particles are very efficient in causing the transformation of nuclei, probably in novel ways. Strong evidence has been obtained of the production of a new type of positively charged particle which has a mass small compared with that of the proton. This may prove to be the positive electron, the counterpart of the well-known negative electron of light mass.

[R.]

Friday, November 10, 1933

KENNETH ROBERT HAY, O.B.E., M.A., M.B.  
*Manager, in the Chair*

N. V. SIDGWICK, M.A., D.Sc., F.R.S.  
*Fellow and Tutor of Lincoln College, Oxford ; University  
Reader in Chemistry ; President of the Faraday Society*

## THE SHAPES OF MOLECULES

MODERN physics has given us a remarkably precise knowledge of the relative positions of the atoms in a molecule, and of the power which the structure has of resisting deformation. The conclusions reached by organic chemists in the last seventy years or so as to the arrangement of the atoms in molecules have been entirely confirmed by the most recent work ; but these conclusions were only qualitative, and the quantitative side—the knowledge of the dimensions and the forces concerned—could not be developed except through the application of physical methods, depending on the use of X-rays, the measurement of spectra, and such physical determinations.

Chemical linkage is of two kinds, electrovalent, as in salts, depending on the electrostatic attractions of charged ions, and covalent, in such molecules as hydrogen, methane and carbon dioxide, which is due to the sharing of electrons between atoms. The structures of electrovalent molecules are largely dependent on their particular conditions, the predominant tendency being for the ions to be packed together as closely as possible ; but in covalent molecules the relative positions of

the atoms are determined by the physics of the atoms, of which the linking electrons form part ; such a molecule constitutes an organised whole, it has an individual shape which persists without much modification through all its states, liquid, solid and gaseous. I shall deal exclusively with molecules of this latter kind.

The first question we have to consider is the size of the atoms. Now we know that an atom has a very complex structure, with a very small heavy particle at the centre, surrounded by light electrons. Exactly how far the electrons extend we cannot say ; modern atomic physics teaches us that as you get further away from the nucleus the chance of finding an electron gets less, but that this electron atmosphere fades away gradually without any sharp limit, like the atmosphere of the earth. Fortunately this complication does not matter to us. What we mean by the volume of the atom is the space from which it keeps out other atoms. As a first approximation we may suppose the atoms to be spheres in contact, the observed interatomic distance being the sum of the radii of the two spheres in question. This conclusion is supported by experiment. For example, the distance between the nuclei of the two atoms in a molecule of hydrogen gas is 0.75 A.U.\*, that between the two atoms in a molecule of chlorine gas is 1.94 A.U. ; we may thus conclude that the radii of the hydrogen and chlorine atoms are the halves of these distances, 0.37 and 0.97 A.U. respectively. If so, the distance between the

\* 1 Angström Unit (A.U.) is  $10^{-8}$  cms. Ordinary atomic models are made on a scale of about 1 inch to the A.U., or 250 millions to 1. This is the ratio of the size of the earth to that of a terrestrial globe 2 inches in diameter.

atoms in hydrogen chloride  $\text{HC}^1$  should be  $0.37 + 0.97 = 1.34$  A.U. It is found to be  $1.27$  A.U., a difference of only  $0.07$  A.U., or about 5 per cent. The values of the atomic radii reached in this way are found to hold remarkably closely for their non-ionised compounds in general, certainly within 10 per cent; the contribution which each atom makes to the link is little affected by the nature

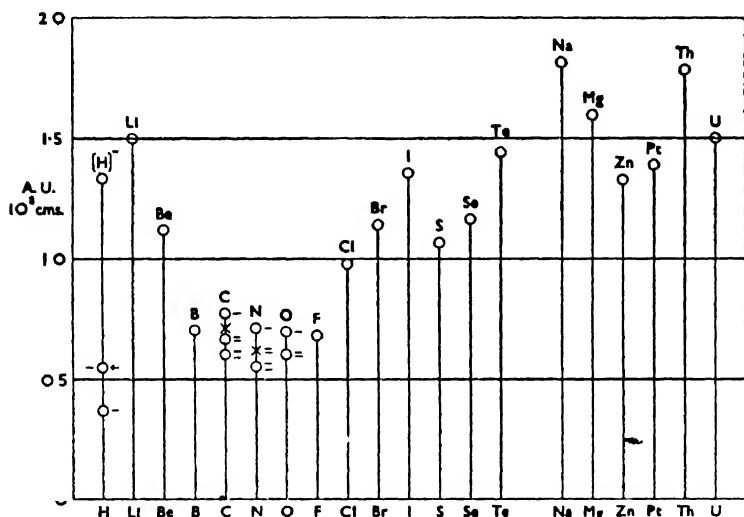


FIG. 1.—Radii of Atoms in Ångstrom Units.

of the other atom. The radii of some important atoms are given in Fig. 1. They all (except the negative  $\text{H}^-$  ion) refer to covalently linked atoms: the different values for atoms such as carbon, refer to different kinds of linkage, single, aromatic, double and triple.

This gives us the size of our building stones. The next question is to ascertain the general styles of architecture adopted. These depend on the numerical valency of the atom, the number of

other atoms which are attached to it directly. This valency can vary from one to eight, the most important classes of atoms are those with valencies of four and six. With a valency of four, the arrangement is always (with the exception of one small group of elements) that which van 't Hoff established for the carbon atom ; the four attached atoms are at the points of a tetrahedron. This has been proved by stereochemical methods for some dozen or more elements, and by the examination of crystal structure for many others, especially for the central atoms in the large group of acids of the type  $H_nXO_4$ , such as the silicates, phosphates, arsenates, chromates, permanganates, etc. The exceptions are some of the transitional elements such as nickel, palladium, platinum and perhaps iron, which have, or at least sometimes have, four groups arranged in a square in the same plane as the central atom. This series of elements is of great interest, but cannot be further discussed here. Otherwise the tetrahedral arrangement of four covalencies is universal. Moreover among the lower covalencies—of two and three—the same arrangement is found. In ammonia,  $NH_3$ , we have rather a flat pyramid, with the nitrogen at the centre of the tetrahedron, and the three hydrogens at three of the four points. The same thing is found with the chlorate ion  $ClO_3$ . With two links, as in water, we have two points occupied, giving a bent molecule. In all these molecules the angles between the valencies are the same, or nearly the same, as they would be in a regular tetrahedron ( $109.5^\circ$ ), except where they are bent out of their normal positions by the requirements of the rest of the molecule, as in cyclopropane, where the angle at the carbon is

reduced by the closing of the ring to  $60^\circ$ , and the molecule shows by its properties that it is very uneasy in that position.

These conclusions for valencies of two and three do not apply in the rather rare cases where the central atom has not a full octet of electrons, as in zinc methyl and boron trichloride; the two are then disposed in a straight line, and three symmetrically at  $120^\circ$  in a plane.

All these compounds contain only single links, but corresponding principles hold for double and triple links, if we suppose that in a double link the two tetrahedra have an edge, and in a triple link a face, in common. Quadruple links, which cannot be realised with tetrahedra, are now known not to exist. In this way we have physical evidence that such molecules as  $\text{O}=\text{C}=\text{O}$ ,  $\text{H}-\text{C}\equiv\text{N}$ ,  $\text{H}-\text{C}\equiv\text{C}-\text{H}$  are linear.

For the higher covalency of six, the octahedral structure of Werner seems to be universal. This was established by stereochemical methods for some eight elements, and by the measurement of crystal structure for a much larger number, in fact wherever it has been looked for.

We have thus established the main principles which determine the way in which several atoms are grouped round one, and we know the distances between the atoms. This enables us to build up a model of any molecule whose chemical constitution is known, with the proper lengths of the limbs, and the proper angles between them.

This, however, is not enough. We want also to know how far this model will "stay put"; how strong it is, and how far it is likely to be altered by the various external and internal forces which act upon it. The most important of these forces is



the thermal agitation. At any temperature above the absolute zero, the molecules of a liquid or gas are moving with a considerable velocity: the molecules of the air in this room travel about sixteen miles a minute. When they hit one another, they naturally do so with some vigour. Then there are various forces of attraction and repulsion between the unlinked atoms of the molecule, which are rather less effective. These forces will tend to modify the relative positions of the atoms in the model to some extent, and we have to consider how far the valency forces between the atoms—the rigidity of the molecule—can resist them. The possible deformations of the molecule can be reduced to three kinds: the twisting of groups around the line of a link, stretching or compressing the links, and bending them.

The evidence of organic chemistry shows that when the link is single, twisting is always possible; a molecule like ethylene dichloride can only occur in one form of substance, so that there are not two possible positions of one half with respect to the other; either one half is rotating all the time, or the molecule remains in the most favoured position. The physical evidence shows that both cases occur. With ethylene dichloride the repulsion of the chlorine atoms favours the position in which they are as far apart as possible, and the molecule is for most of the time in or near this; but the impacts of other molecules push it to some extent out of this position, and it oscillates round it like a pendulum, and no doubt when it gets an extra heavy blow swings right round. The recent results of X-ray analysis of crystals show that even there, if they are not too cold, light groups, like methyl  $\text{CH}_3$ , are in a state of

continuous spin. At any rate it is clear that this rotation round the line of a single link is always possible, and that the valency forces offer no opposition to it. On the other hand no such rotation can occur round the line of a double link. In this case the change from one form to the other is only possible by a considerable expenditure of energy, and is of the nature of a definite chemical reaction. Our model must therefore be freely movable round its single links, but quite stiff in its double links

With regard to the stretching and compression of the links we have a great deal of information, derived from the absorption spectra. This shows that the resistance is strong; it does not vary very much with the nature of the atoms, and is about twice as great for a double, and three times as great for a triple as for a single link.

Our data for the bending of the links are still very scanty, but from what we have it is evident that it is easier—about five times as easy—to bend a link as to stretch it to the same extent. The values of the constants show that in a gas or liquid at the ordinary temperature, while the molecules are spinning as a whole, and also, to a considerable extent, the parts of molecules which are united by single links, there is very little bending of the valencies and hardly any stretching.

We should now be in a position to build up our model. We know how far the centres of the linked atoms are apart, and we know the angles at which the atoms are to be joined to a central atom. We also know when the attachment should be made so as to allow of free rotation and when it should not; and we have some idea how stiff the joints should be. With the help of a series of

balls of radii proportional to those found from the interatomic distances, and bored for fitting together at the proper angles, we can construct our model quite easily. But when we have done this, we find it is not big enough. From the density of the substance in the liquid state we can calculate the volume which our model must occupy, and when we test the model we find it does not fill it. The truth is that two atoms which are not chemically linked cannot get as near to one another as two which are. For example, in liquid hydrogen, two linked atoms of a molecule have their centres  $0.75$  A.U. away. But the next hydrogen, of another molecule, is more like  $2$  A.U. away. When we made use, as everyone does, of a series of balls to represent the atoms, we were really assuming that the domain of the atom extends no further on the unlinked than on the linked side, and this is quite untrue. Instead of spheres, we ought to use a sort of pear-shaped solid, with the stalks joined together. Or perhaps it would be better to use children's indiarubber air balls, because it is clear that these figures are much softer on the outside than on the inner side, and the thickness of the imaginary envelope varies very much with the conditions. This separation of the unlinked atoms can be seen in almost any X-ray picture of a non-ionised substance; in a salt the powerful forces between the ions greatly reduce the thickness of the envelope.

This difference between the size of what I may call the internal and external radii of an atom does not apply only to the distances between the atoms of different molecules; if it did, it would be of less importance. It applies equally to the distances between two atoms of the same molecule, if they

are not chemically linked to one another. Its cause is quite clear. The electrons of the atoms are all negatively charged electrically and therefore tend to repel one another. In their orbits they also behave as small magnets. When the covalent link is formed, the electrons so arrange themselves that their magnetic fields make them attract one another, and it is this attraction which leads to the chemical combination. In the complete saturated molecule all the magnetic moments of all the electrons neutralise one another. But the electrons still retain their electric charges, and as these are all negative, they repel one another.

In conclusion I may draw attention to a remarkable point in the structure of carbon and its compounds. Organic chemists have long recognised two main classes of carbon compounds, the aliphatic, derived from the saturated hydrocarbons, like methane and ethane, and the aromatic, derived from benzene. The two classes are markedly distinct in chemical properties. When we examine the shapes of their molecules, we find that here too there is a marked distinction. The saturated hydrocarbons (and the aliphatic compounds generally) are all built on the tetrahedral model: the distance between two attached carbon atoms is always 1.54 A.U., the angle is always about  $110^\circ$ , the heat of formation of the C-C link is about 70 k.cals. If we imagine this structure continuously extended, we arrive at a molecule in which every carbon atom is joined to four others, except the outermost, which carry hydrogen atoms; but if we make the molecule infinitely large, the amount of hydrogen will be negligible. This is exactly what we have in diamond. The whole crystal is one gigantic molecule: every

carbon is joined to four others: the valency angles are all  $109.5^\circ$ , the C-C distance is 1.54 A.U., the heat of linkage is 75 k.cals. The benzene structure on the other hand has been shown to be plane, not only the 6-atom ring itself, but also the atoms directly attached to it, as in hexamethyl benzene. The distance between the carbon atoms in the ring is different: it is 1.42 A.U. The angle is  $120^\circ$ . The distance between one

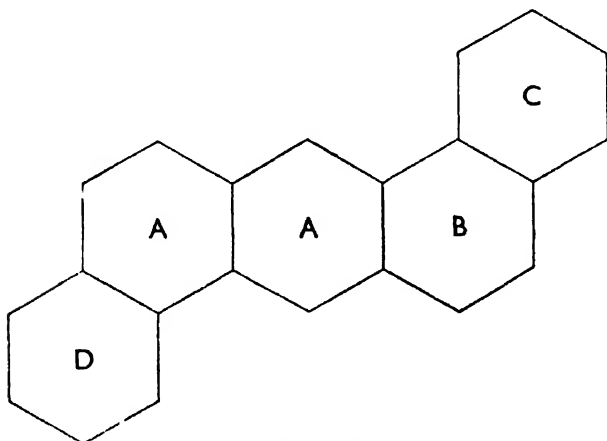


FIG. 2 Dibenzanthracene.

molecule and the next (owing to the electron repulsion already discussed) is about 3.5 A.U. In the more complicated derivatives with several rings fused together—naphthalene with two (*a,a*), anthracene with three (*a,a,b*), cymene with four (*a,a,b,c*), and dibenzanthracene (Fig. 2) with five (*a,a,b,c,d*)—the same arrangement has been shown to hold; plane distribution, angle  $120^\circ$ , distance between linked carbon atoms 1.42 A.U., distance to the next molecule 3.5 A.U. If we imagine this style of architecture indefinitely extended we arrive at a giant molecule forming a plane sheet

one atom thick, made up of continuous hexagons, like wire netting, with all the angles  $120^\circ$ , the distances between neighbouring atoms 1.42 A.U. This is what we have in graphite, which is entirely composed of sheets of this kind, and the distances between the sheets, which are really separate molecules, is 3.4 A.U., just as in benzene or anthracene. Thus the two most important groups of organic compounds are seen to lead up to the two allotropic forms of elementary carbon, diamond and graphite.

[N. V. S.]

Friday, November 24, 1933

SIR HENRY MIERS, M.A., D.Sc., LL.D., F.R.S.  
*Manager and Vice-President, in the Chair*

SIR WILLIAM BRAGG,  
O.M., K.B.E., M.A., D.Sc., F.R.S., M.R.I.  
*Fullerian Professor of Chemistry*

## LIQUID CRYSTALS

THERE are substances which are liquid in their mobility and crystalline in their optical behaviour. The latter property suggests that there must be some degree of arrangement of the component molecules, and the former that this arrangement is readily disturbed though it may be as readily renewed. Such substances are generally described as "Liquid Crystals." It is argued, especially by Friedel, to whom we owe so much of our knowledge of their properties, that the title is bad, because the substances are neither perfect crystals nor perfect liquids. Friedel would call them mesomorphs, which is much more logical, since the conditions to be described are intermediate between other conditions that are well known. The term "liquid crystals" is, however, simple and suggestive, and those who use it are not likely to be misled.

The first to give any full and clear account of the properties of liquid crystals was O. Lehmann.\* Following him a number of investigators have attacked the general problem from various sides,

\* O. Lehmann, "Uber fließende Kristalle," *Zeit. f. phys. Chem.* IV. 1889.

Vorlander, Schenck, Friedel, Grandjean, Mauguin, Oseen and others. Quite a large literature has grown up round the subject. Friedel has given a full account of his experiments in the *Annales de Physique*.\* The present state of knowledge may be inferred from the account of the General Discussion on Liquid Crystals and Anisotropic Melts held by the Faraday Society in April, 1933.†

The characteristic properties of liquid crystals are connected with the peculiar form of their molecules. These are relatively complicated structures possessing a common feature in their lengthy, chain-like form. It is not surprising that such molecules should sometimes exist in a state intermediate between solid and fluid. If the form and influences of a molecule can be represented approximately by a sphere, an assemblage of such molecules will resolve itself into individuals at some definite temperature. That is because all the links with neighbouring molecules are similar and break down together. But when the molecule is relatively long and narrow, the linkages in different parts of it may be of different strengths. Some may be broken at a lower temperature than others. There must then be one or more intermediate states of greater but not complete mobility. A sufficiently high temperature will bring about the dissolution of the remaining molecular associations, and then a truly liquid state is reached. Though the intermediate phases lack the complete ordering of the crystal, that which remains has necessarily its optical effects.

It is an important fact that the changes from solid to liquid crystal, and from liquid crystal to

\* *Ann. de Physique*, 9 S. Vol. XVIII, p. 273, 1922.

† *Faraday Soc. Trans*, Vol. XXIX, p. 881, 1933.



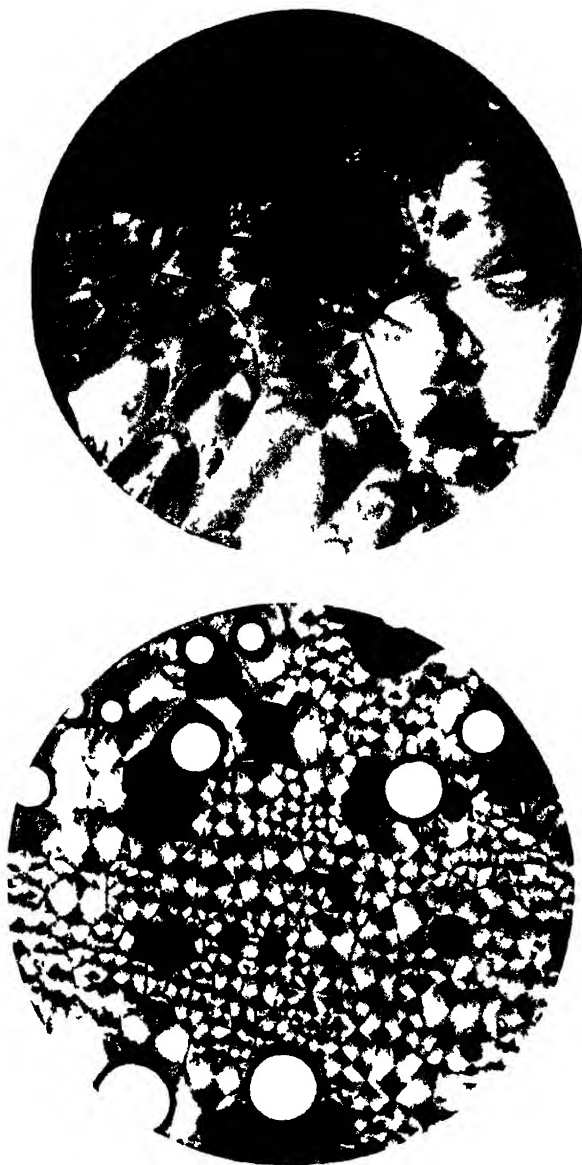


PLATE I.—Enlarged micro photograph of a liquid crystal (see text). A Nicol prism is used as analyzer, there is no polariser. The substance is ethyl para-azoxybenzoate temperature  $414^{\circ}\text{C}$ – $120^{\circ}\text{C}$ . Notice the polygons and the appearances of cones within them. The white circles are air-bubbles the gray portions are liquid. The diameter of the original before magnification is three-quarters of a millimetre.

liquid are as sharp and definite as the change from solid to liquid in the more general case.

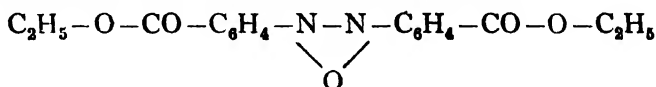
These optical effects possess in many cases a singular beauty, in respect both to colour and to form (*See Plates I, II and III\**). Most of them, but not all, can be explained in comparatively simple terms which, however, are rarely described in treatises on optics. Writers have confined themselves to true crystals and true liquids and the more complicated problem is discussed only in isolated papers. In what follows a brief account is given of this peculiar optics and of the consequent inferences as to the liquid crystal structure.

Friedel divides liquid crystals into three classes : in his own words, there are three mesomorphous phases. The first of these he calls "smectic," thereby implying a parallelism with the soaps. Their special feature is their stratification. In each layer the molecules are arranged side by side, like corn in a field, the thickness of the layer being the length of the molecule. In the case of the soap bubble or film, we have such layers forming the surface inside and out. The side to side attractions of the molecules bind them together, so that the film has a certain surface energy of tension. If the film is made to grow larger in extent, other molecules of the sodium oleate slip into their places and increase the area. If the film contracts, molecules drop out and go back into the liquid.

Let us suppose now that such layers are formed in the substance ethyl-azoxybenzoate, which shows the smectic phenomena very well. Each sheet is very flexible. If such a sheet could be suspended in space, free from gravity, it would take the form

\* The photographs are due to W. J. Green.

of a perfectly flat surface because the molecules would tend to lie parallel to one another. Their side to side attractions are relatively strong. If bent, it would straighten itself out again. If a number of such sheets were put together like the leaves of a book, they would tend to adjust themselves further, so that the ends of the molecules on the face of one sheet fitted exactly in some characteristic way on to the ends of the molecules on the next sheet. In this way the solid crystal would be formed, in which there is arrangement and regular repetition in every direction in space. But in the smectic state the temperature is high enough to ease the bonds between sheet and sheet, and yet not high enough to break up the sheets themselves. A single sheet does not necessarily behave like a separate crystal: it is rather to be considered as a two-dimensional fluid.



Ethyl para-azoxybenzoate

Solid  $-114^{\circ}$ —smectic  $-120^{\circ}$ —liquid

A sheet of this nature can slide without hindrance on its neighbours. When a film of the above-mentioned substance is stretched over a small hole in a plate, the condition of parallel layers is in fact arrived at. It can also be reached when the substance rests on a plate, but unless the plate is carefully prepared it is apt to be interfered with by local attachments, as will be seen presently. In the simple form the substance may be examined in polarised convergent light, and will show the usual rings. With the aid of a quarter-wave plate it can be shown by well-known methods that the arrangement simulates a positive

crystal. The full structure of the crystal is not realised because the separate sheets are not properly adjusted to each other. That, however, does not affect the examination in convergent light, which requires only that the axis of the beam shall be perpendicular to the layers. The experiment shows that the substance behaves like a positive crystal, such as quartz. In other words the frequency of the light vibrations perpendicular to the layers (and parallel to the molecules) is less than the frequency when the vibrations are not perpendicular thereto. This is to be expected, because it is always found that vibrations along an extended molecule are slower than those across it. The simple stratification lends itself also to study by X-rays, when it appears that the thickness of the layer agrees closely with what we know of the length of such molecules, based on exact X-ray measurements of other organic molecules. Friedel\* gives the value 19.9 Å. In the solid crystal the thickness of the layer is found to be 16.2. The difference is due to the fact that in the layers of the solid the molecules are inclined and not upright as in the liquid crystal.

In general, however, the substance, when placed between glasses, as is usual when examination is to be made under the microscope, and when raised to the proper range of temperature, or cooled from the melt, does not assume the simple form. The strata are crumpled. Attachments between substance and glass are strong, and at various points these attachments compel the arrangement of the molecules in different directions. The general arrangement has to accommodate itself to enforced conditions in various

\* Comptes Rendus, Vol. CLXXX, p. 265, 1925.

places. Moreover, nuclear associations of molecules are formed at various points in the liquid when it is passing into the liquid crystals phase ;

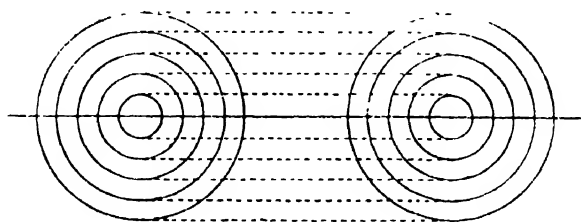


FIG. 1.—Section of an anchor-ring in layers, which constitute a particular series of Dupin's cyclides.

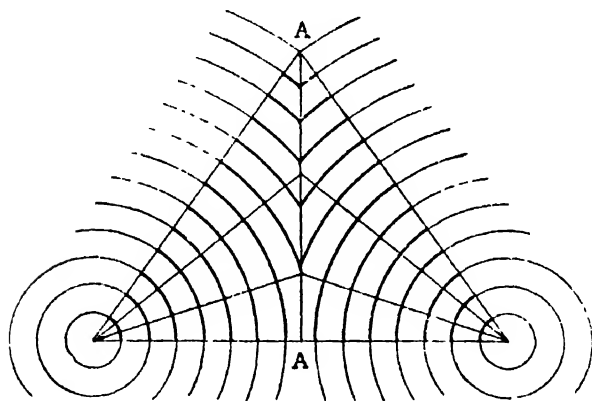


FIG. 2.—An axis AA is now added to the ring of Fig. 1. Every straight line drawn from any point on AA to any point on the axial circle of the ring meets every layer at right angles. In this figure emphasis is laid on those parts of the layers which lie within the cone of which the upper point A is the vertex and the axial circle is the circumference of the flat base. Within the cone the layers are in equilibrium with each other. How one cone can be fitted to another is explained in the text.

and these must be fitted to one another as they grow and meet together. There is something like the contortion of strata in a geological formation ; but the smectic arrangement is simpler, because

the layers while preserving their thickness exactly, can slide easily over one another and so can adjust themselves to surface conditions.

The optical peculiarities of the smectic state are caused by these contortions of the strata. We have therefore to consider in the first place the forms which the strata assume, and in the second their effect upon the transmission of light.

From direct observation it can be inferred, as will be seen presently, that the surfaces of the strata form series of the "cyclides" examined long ago by Dupin and known by his name. We must therefore consider their chief properties.

The locus of the vertices of the circular cones (cones of revolution) passing through a given ellipse is a hyperbola which passes through the focus of the ellipse and lies in a plane perpendicular to that of the ellipse. Conversely the ellipse is the locus of the vertices of circular cones passing through the hyperbola. The ellipse and the hyperbola are described as "focal conics."

Surfaces can be drawn which are at right angles to all the straight lines which pass through both conics. These are Dupin's cyclides. They are peculiar in that any pair of surfaces is equally separated everywhere, the distance of separation being measured along the common normal. Obviously this makes it possible for the surfaces to coincide with the surfaces of sheets of uniform thickness.

It is easy to form an idea of the arrangement by considering a simple case. The ellipse may become a circle, in which case the hyperbola becomes the axis of the circle, that is to say, a straight line passing through the centre of the circle and perpendicular to its plane. The

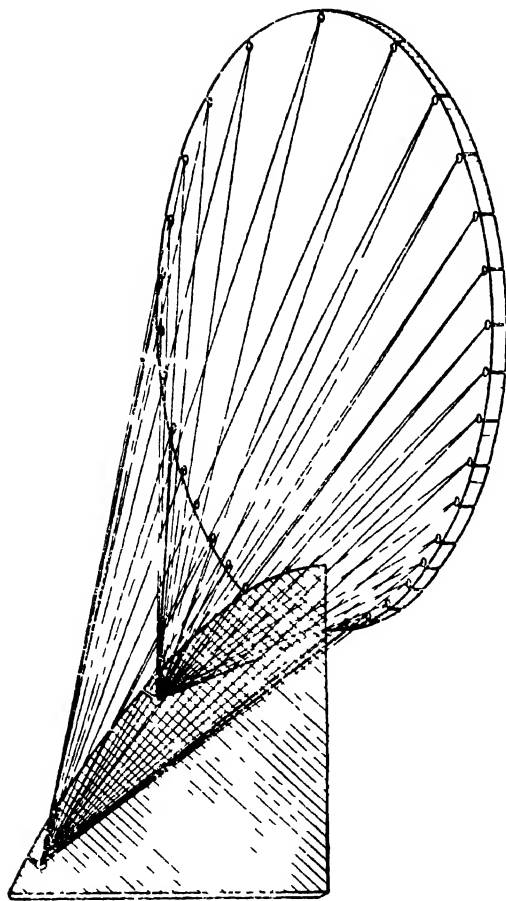


FIG. 3.—A drawing of a model made to illustrate the structure of the interior of an oblique cone containing the smectic substance. The two sheets of zinc are cut into the form of an ellipse and part of a hyperbola, and are fastened together so that their planes are perpendicular to each other and each curve goes through the focus of the other. Slots are cut as shown, and strings join two points on the hyperbola to a number of points on the ellipse. If the ellipse were made into a circle, the hyperbola would become the axis of the circle as in Fig. 2. The strata, having the form of Dupin's cyclides, intersect every one of the strings at right angles.

cyclides become "anchor-rings" or "tores," intersected at right angles by every straight line that meets both circle and axis. The construction is shown in Figures 1 and 2.

When this simple case occurs in the liquid crystal the strata are bounded by a succession of anchor rings equally separated. The straight lines that meet both circle and axis are perpendicular to the strata and therefore parallel to the long dimension of the molecule. As has been said above, the substance behaves like a uniaxial crystal, the axis lying along the molecule. The straight lines show therefore the direction of the optic axis at every point, being parallel to the molecules round about the point. It must not be supposed, however, that each such straight line is a chain of molecules; if that were the case converging lines of molecules would "jam" into one another.

It will be observed that no two of the straight lines intersect. We may pass from this special case to the general by imagining the circle to become an ellipse and the cones to be pushed over to the side as in Figures 3 and 3a. The anchor rings become distorted, but the characteristic properties of the cyclides are still maintained. Every straight line that meets both ellipse and hyperbola is normal at all points to a series of surfaces, and still any two of the surfaces are everywhere separated by the same distance, measured along the common normal.

If now we take any two points on the hyperbola, of which one may be the focus of the ellipse, and draw from each of them straight lines to every point on the ellipse, we include a region bounded by two cones, or in the special case one cone and



its flat base, which can be divided by Dupin cyclides into a series of sheets of uniform thickness ; and at all points on the surface of the space the sheets are perpendicular to the generators of the cones.

We are now going to see how, in imagination, we can divide a solid mass of material such as that which lies on the microscope slide, into separate blocks, in each of which the substance

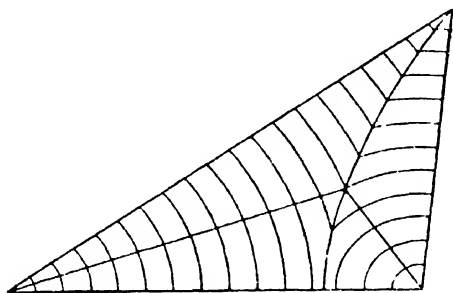


FIG. 3a.—A section of Fig. 3 in the plane of the hyperbola, showing parts of cyclides. Compare this with Fig. 2. The complete cyclide which in Fig. 2 was a uniform ring, the so-called "anchor-ring," is now thicker on one side than on the other.

is arranged on one or more sets of cyclides, while all the blocks can be fitted together so that the stratification runs continuously through the whole.

If two such conical regions are made to touch along a common generator, the cyclides in one region may be looked on as continuations of the cyclides in the other, though they come into contact only at the common generator. Any pyramidal space can be divided into cones, large ones in the centre, smaller cones partially filling up corners that are left, and still smaller cones

filling up corners that are still left, and so on. The pyramidal space can then be further sub-divided into strata of uniform thickness by sets of cyclides, one set to each cone, which all fit on to one

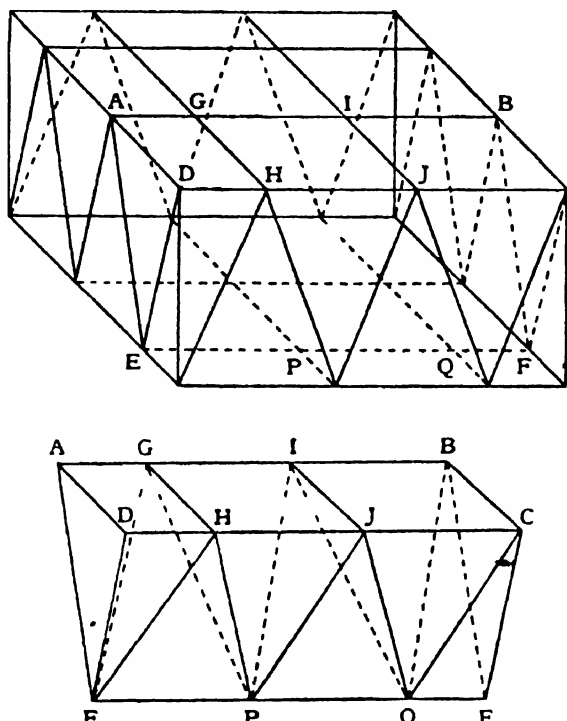


FIG. 4.—The rectangular block is divided by saw-cuts into wedges; the division being made in two ways, parallel to two of the edges of the block. Below the block is shown one of the wedges obtained by cutting parallel to AB. The second set of cuts, parallel to AD, divides this larger wedge into pyramids such as P(GHIJ) and smaller wedges such as IJPQ.

another, and meet at right angles the straight lines drawn from the vertex to all the points on the polygon forming the base. In each of the cones the vertex and the focus of the ellipse forming its

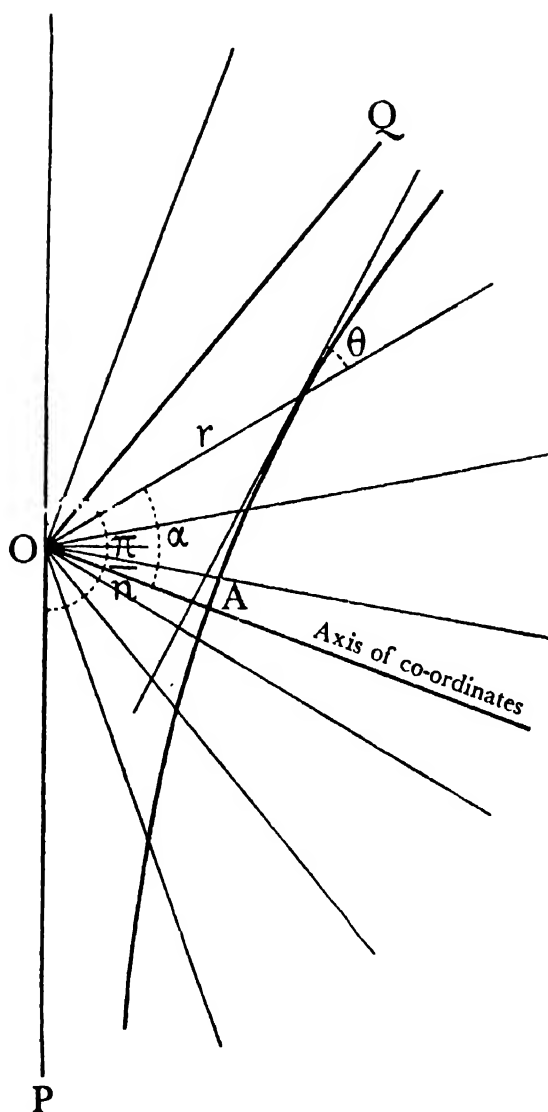


FIG. 5.—The curved line shows the path of the extraordinary ray in a medium in which the axial direction at any point is directed towards O. The axes and the path lie in one plane.

base are the two terminal points on the hyperbola belonging to that cone. Since all the hyperbolæ lie on planes that are perpendicular to the bases of the cones, which bases are co-planar, and all pass through the vertex of the pyramid, the major axes of the ellipses all pass through the projection of the vertex on the basal plane.

A solid block can be divided into two sets of pyramids, half of which have their bases on each one of two opposite faces and vertices on the other, together with certain wedge like spaces. This is readily seen if we consider such a division as is indicated in Figure 4, where the pyramids are, for simplicity, set on square bases; and it appears that besides the pyramids there are wedges or tetrahedra such as IJPQ. Pyramids and wedges account for the whole. Now the top and bottom edges of each wedge can be looked on as portions of a pair of focal conics, and the space inside the wedge can be divided by cyclides which meet the other four edges at right angles and therefore pass continuously into cyclides in the adjoining pyramids. The top and bottom edges must have at least some small curvature. If straight lines be drawn from every point on the upper edge to every point on the lower, they are all normal to the set of cyclides which divide the space inside the wedge into layers of uniform thickness.

Thus the whole of a solid block can be divided into uniformly thick contorted layers by Dupin cyclides belonging to a number of different sets which, however, fit on to each other perfectly.

We have next to show that the optical effects are consistent with such an arrangement, and in fact establish its existence.

In a solid crystal the direction of the axes is constant throughout. In a liquid crystal this is not the case. Fortunately for our convenience in solving the new problem, there is only one axial direction at each point, namely, that which is perpendicular to the layer; it coincides with the straight line passing through the point and also through the two focal conics. We may divide into two parts the problem of the path of a ray through a liquid crystal. Consider first the case when a continuous change in the direction of the crystal axis is taking place in the plane containing the path of the ray. Let that plane be the plane of the paper and let the axes be directed towards the point O in Figure 5. Clearly a vibration which is perpendicular to the plane is always perpendicular to the axis wherever it is, and is never deflected. But a vibration in the plane of the diagram is that of an "extraordinary" ray and suffers continuous deflection. Its path was calculated by Grandjean\* who showed that it moves on the curve  $r \cos n \alpha = a$ , where  $r$  and  $\alpha$  are polar co-ordinates, O being the pole;  $n$  is the ratio of the refractive index of the extraordinary to that of the ordinary ray, and  $a$  ( $= OA$ ) is a constant. A proof is given in the appendix to this discourse. If  $n=1$ , the curve becomes a straight line, as it ought to do, since the substance would then behave as if isotropic, and a ray of light would go straight through. The curve in the figure has the two straight lines OP and OQ as asymptotes, and the angle  $POQ = \pi/n$ . An extraordinary ray approaching along a line originally parallel to OP but not directed at O is finally deflected along OQ. At the beginning and the

\* Bull. Soc. Min., Vol. XLII, p. 42, 1919.

end it is very nearly an ordinary ray. To sum up, ordinary rays consisting of vibrations normal to the diagram suffer no deflection, but extraordinary rays do.

Next we consider a ray passing through a region where the direction of the axis is changing continuously but is always normal to the direction of the ray. Such a structure may be termed a twisted or helicoidal structure. In any plane which is normal to the ray, the direction of the axis is the same at every point but the direction changes continuously along the ray, as happens in a pack of cards to which a twist has been applied about an axis perpendicular to the plane of the cards.

It is not to be expected that a polarised ray would maintain unchanged the rectilinear character of its vibration during its passage through such a medium; in fact, Maxwell's equations of the electro-magnetic field cannot be satisfied by so simple an assumption. But if we try an elliptically polarised ray and suppose that the axes of the ellipse follow the twist, we find that the equations are satisfied for certain degrees of ellipticity and corresponding velocities. We have therefore found the solution of our problem. The proof of this general statement is given in the appendix; a particular case only is of importance to us here. In cases with which we are dealing the wave length  $\lambda$  is very small compared to  $p$ , the pitch of the screw. As Mauguin showed in the case of the nematic substances which we shall examine later, it is not possible to twist the medium so much as to make  $\lambda/p$  anything but a small fraction. It appears that the ellipticities are then small, and the result can be expressed as follows :—

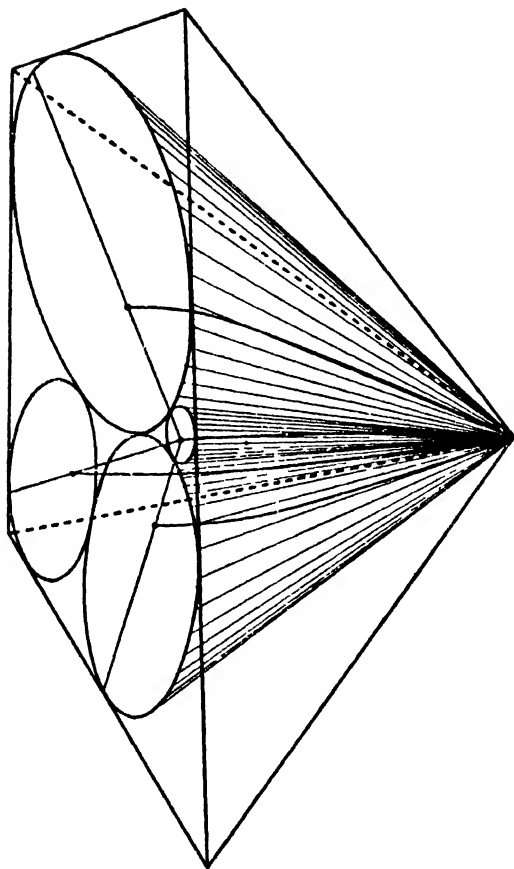


FIG. 6.—The arrangement of a set of cones within a pyramid. It follows closely the actual arrangement within a polygon near the bottom and on the left of the lower photograph Plate I. It is to be remembered that the apparent cones in the photographs of Plates I and II are not the cones of this figure though connected with them. Some lines are drawn in the figure in order to outline the cones. The hyperbolæ belonging to the various ellipses meet at the vertex of the pyramid. The vacant spaces in the pyramid are filled with smaller cones or portions of cones.

Let  $K_1$  and  $K_2$  be the effective specific inductive capacities across and along the axis. Let  $c$  be the velocity in space, and  $c/\sqrt{K}$  the velocity in the medium: let  $\lambda_0$  and  $\lambda$  be the corresponding wave lengths. Let  $a$  and  $b$  be the axes of the elliptical vibration. Then *either* :—

$K = K_1$  to the second order of small quantities and  $b/a = 2\lambda K_1/p (K_1 - K_2) = 2\lambda_0 \sqrt{K_1}/p (K_1 - K_2)$  or  $K = K_2$  and  $a/b = 2\lambda_0 \sqrt{K_2}/p (K_2 - K_1)$ .

It appears therefore that in the twisted medium two elliptical vibrations can travel without change of form, each with its special velocity. When the twist is small we may assume that incident light is resolved into two linear vibrations, the ellipticity being negligible. These vibrations, however, follow the twist so that the vibrations at any point are always along and perpendicular respectively to the crystal axis at that point. If exactness were necessary, we should have to recognise that incident light is always resolved into two elliptic vibrations of different ellipticities travelling with different speeds. For instance a polarised ray, in which the vibration is parallel to the crystal axis at the surface, is resolved into two elliptic vibrations which travel at different rates. The major axis of the larger lies in the direction of the incident vibration, that of the smaller is perpendicular to it and is equal to the minor axis of the larger. The two rotate in opposite directions. At regularly spaced depths in the medium the two again combine into a linear vibration.

It is to be observed that this effect is practically independent of the wave length. The rate of rotation for all wave lengths is that of the mechanical structure.



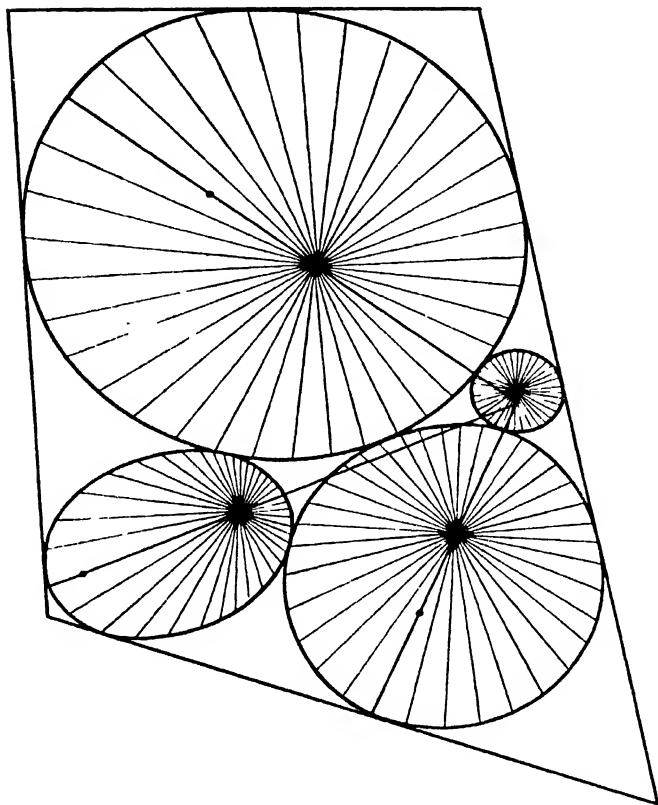


FIG. 7.—This shows the base of the pyramid in Fig. 6 : and the axial directions radiating from every focus at the base of the hyperbolæ (see Fig. 6). The axes of the ellipses all meet at a point which is the projection of the vertex of the pyramid upon the base.

Any axial direction can be brought into coincidence with any other axial direction by a rotation in the plane containing the direction of the ray combined with a rotation about the ray. Thus we are able to say, as the result of the two cases considered, that the ordinary ray goes through the liquid crystal without any change in the direction of its path, no matter how the axis of the crystal alters its direction, provided that the latter alteration is continuous. The direction of the vibration changes in such a way that it is always perpendicular to the axis of the crystal. On the other hand the extraordinary ray, though behaving like the ordinary ray in all other respects, continuously changes the direction of its path when there is any continuous change in the orientation of the crystal axis, which has a component in the plane containing the ray and the axis.

We can now proceed to examine the appearance of a smectic substance in the light of what we have just proved. Let us consider the photographs in Plate I. These are typical of the great variety of appearances presented by a thin layer of ethyl azoxybenzoate. It is in the smectic state, the temperature being held between the limits  $114^{\circ}\text{C}$  and  $120^{\circ}\text{C}$ . The microscope is focussed on the upper surface of the layer and is viewed through an analysing Nicol. There is no polariser. We observe at once the assemblage of polygons each with its content of ellipses. If we suppose that the substance is crumpled up into a combination of sets of cyclides as explained above, and also that these are grouped in cones, pyramids and wedges (see Figures 3, 3a, 4, 6 and 7) then the arrangement of the optic axes in the surface of the layer will be as in Figure 7; with infinite possi-

bility of variation in the number and sizes of the ellipses. The molecules on the surface lie always on straight lines, which show the directions of the crystal axes at every point, and in each ellipse radiate from the focus to the circumference.

At every point the vibration in the ordinary ray as it emerges is perpendicular to the radius vector from the focus. The original beam divides into two on entering the substance, as usual, but the

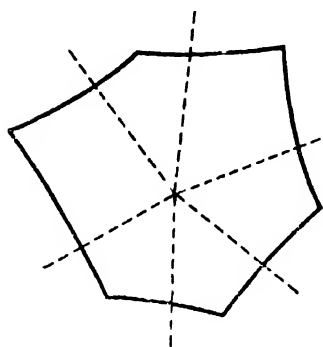


FIG. 8.—This shows the disposition of polygon edges in one face of the lower left hand portion of Plate II with respect to polygon edges in the other face.

extraordinary ray quickly goes astray. If it gets through, its vibration is inclined to the radius vector, but its appearance is quite irregular. On the other hand the ordinary ray appears uniformly at all parts of the field and gives the clear picture which is seen in the microscope. The analyser transmits vibrations parallel to its principal plane, and consequently each ellipse is crossed by a

shadow which culminates at the focus. The central line of the shadow is parallel to the principal plane of the Nicol. It will be observed that when a polygon includes several ellipses, the major axes of those ellipses are all directed towards a single point, which, as already explained, is the projection upon the polygon of the vertex of the pyramid standing on the polygon. The vertex lies on the opposite face. When the microscope is adjusted so that the lower face is in focus, it is found that the point on which the major axes of

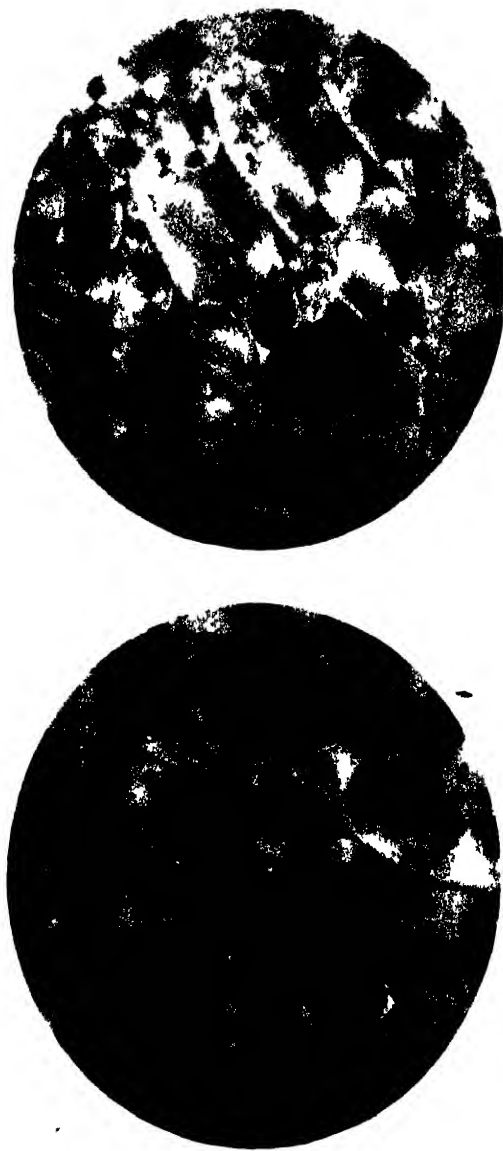


PLATE II — Two photographs of the same portion of a smectic preparation, but in the one on the right the upper surface is in focus, and in the one on the left the lower. In the lower left hand portion of the photograph on the right is a fairly regular six-sided polygon, of which the centre is occupied by an ellipse which is nearly a circle. A number of smaller ellipses lie within the same polygon. The axes of all these ellipses are directed to a point. When the other surface is brought into focus this point is seen to be the meeting place of six polygon edges, as is shown by the illustration on the left. This point is the vertex of a pyramid standing on the six-sided polygon. The six lines that meet in a point on one face are the upper edges of wedges of which the lower edges are the sides of the polygon on the other face. They are separately at right angles to these lines because they all come from the same point, and are viewed at right angles to the plane of the surface.

the ellipses converge melts into a point where a number of edges of polygons meet. This is illustrated in Plate II and Figure 8.

The polygon edges of Plate I vary in shade, some being light and some dark. It will be observed that the dark edges are more or less parallel to the middle line of the shadow in each

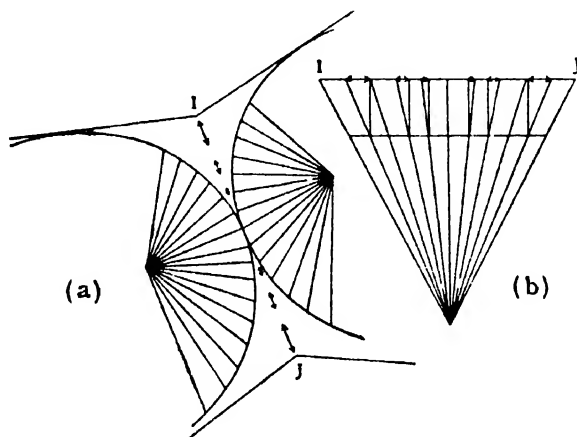


FIG. 9.—This shows how the crystal axes in the edge of the wedge IJ are at right angles to the axes inside the ellipses where they touch the edge (Fig. 9a). About the middle of the edge, the axes are often vertical. This is very often the case in the upper illustration in the Plate. The light from below gets through on this line without being resolved, and is only half darkened by the analyser. The section of IJ marked off by arrow-heads represents the direction and relative values of the axial projection on IJ; the manner of doing this is shown in Fig. 9b.

polygon; and therefore also to the crystal axis along the edge. This is readily understood when we remember that the side of the polygon is the top edge of a wedge. Inside a wedge the axes run from every point on the top edge to every point on the bottom edge. Along the top edge the projection of the axes is therefore parallel to the

edge as shown in Figure 9. Somewhere in the edge, however, there is a point, unless the wedge is very skewed, where the axis is perpendicular to it, being the shortest distance between the top and bottom edges. At this point the extraordinary becomes equivalent to the ordinary. There is no separation when the light enters the medium, and the analyser does not quench it entirely. A black edge then shows a white spot in the middle.

From the general and close agreement between theory and observation, we may surely conclude that the smectic substance is indeed arranged in strata which take the form of Dupin's cyclides. There are however any number of other geometrical arrangements of sheets of uniform thickness. There must be a reason why the cyclides are preferred, and it must be based on energy considerations. A soap film stretched on a frame takes a form involving minimum energy; if the pressure is the same on both sides the total curvature is everywhere zero, and the edges comply with enforced boundary conditions. In the same way the strata in the smectic state must also, while obeying boundary conditions, arrange themselves so that the potential energy is a minimum.

Simplicity and symmetry imply less storage of energy than unnecessary complication and lack of symmetry. Let us consider possible methods of arrangement in declining order of symmetry.

If strata, originally plane and parallel to each other, are forced out of this arrangement, which is the simplest of all, they must tend to take the cylindrical form which comes next in simplicity. If the disturbing influences are complicated, the various attempts to adopt the cylindrical form

must in some way be accommodated to each other. A set of strata of even thickness, bent into cylindrical form, is so grouped round the axis of the cylinder that the normals to the strata at all points intersect the axis at right angles. It is not possible, however, to divide a mass of the smectic substance into cylindrical groupings of this kind, the various groupings cannot be made conformable with each other.

In the next order of simplicity the normals to the strata still meet in a line, but are inclined to it, forming cones of revolution, the vertices of which are points on the line, the inclination being constant in all directions radiating from any point on the line. This is illustrated in various preceding figures, for example Figure 3. Each cone is symmetrical about its axis.

It is this arrangement which is adopted. Every normal to the strata is anchored on two lines which are focal conics. Every boundary surface of the strata is as symmetrical as possible, being at right angles to series of cones of revolution; and the various sets of surfaces are conformable to each other as we have seen. The cyclides are the only surfaces which fulfil these conditions. The geometry of the cyclide was considered by Clerk Maxwell\*, who pointed out that if the rays in a beam of light pass through two focal lines, the lines are necessarily parts of focal conics. The wave surfaces are equally spaced cyclides to which all the rays are normal.

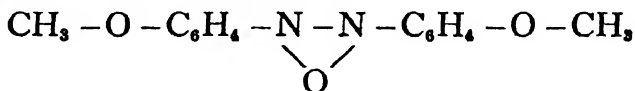
A useful list of substances which may exist in the smectic state is given by Friedel in the paper already referred to.† The azoxybenzoate is often

\* Collected Researches, Vol. II, p. 144.

† Ann de Physique, 9 S., Vol. XVIII, p. 273, 1922.

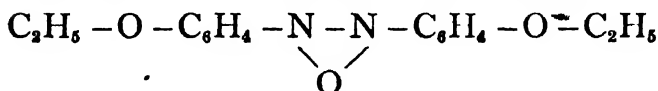
taken as typical, as it is easily made to show all the smectic characteristics.

The second of the three classes of liquid crystals, outlined by Friedel, was called by him "nematic," from the singular appearance of mobile threads, either free in the interior of the substance or attached more or less to the bounding plates. These have none of the focal conic structures of the smectic substances, having in fact no stratification. They possess optical properties, however, and therefore some degree of molecular arrangement. What that arrangement is may well be inferred from a recent determination of the solid crystal structure by Bernal and Crowfoot.\* Para-azoxyanisole and para-azoxyphenetole are typical nematic substances.



Para-azoxyanisole

Solid - 116° - nematic - 113° - liquid



Para-azoxyphenetole

Solid - 135° - nematic - 165° - liquid.

X-ray analysis shows that the molecules in the solid lie parallel to one another, but cannot be clearly separated into layers. They interleave one another, or, to use the description by the authors referred to, they are imbricated. Certain indications found on the X-ray photographs show also that the degree of interpenetration is not sharply defined but is variable about an average value. Since the change from solid to the

\* Faraday Soc. Trans., Vol. XXIX, p. 1032, 1933.



“ liquid crystal ” form is so easy, there cannot be much variation in arrangement or bindings, and the natural inference is that, even more in the latter than in the former phase, the interpenetration lengthways is variable and easily effected. We should therefore conceive of the substance as owing its mobility to the facility with which the molecules can be drawn past each other, while retaining a strong tendency to acquire or retain a parallelism between the long dimensions of the molecules and the direction of drawing.

Another striking characteristic of the nematic state is the tendency for the molecules to be attached sideways to the slide or the coverslip. If once a solid crystal has formed between the two glass surfaces, it is difficult to remove all traces of its having done so. The substance may be completely melted and allowed to return to the nematic state, whereupon it will recrystallise more or less according to the same plan as before. The melting does not remove all the molecules adhering sideways to the glass, and enough remain to redirect the molecules in their former orientation in each separate part of the preparation. In the microscope, when the Nicols are crossed, the appearance is that of a map in which the different countries are differently tinted, because the general direction of the molecules in each part is peculiar to that part. In each part the direction may be the same right through the preparation from one glass surface to the other, especially if the layer is thin. If one or both of the Nicols are rotated, the alternations of light and dark are the same as if the preparation were a section of a uniaxial real crystal. And yet the substance is liquid (Friedel, *loc. cit*). If particles of dust or

other intrusions wander through it they move freely, while the optical effects are unchanged. The orientations of the molecules are governed by those on the surface, and even if there is a stream flowing, they do not diverge from the common orientation of the section in which they are. But, if they move into another section, they change the old orientation for a new one.

Suppose now that the cover slip is moved, either by translation or by rotation with respect to the slide. In many places it must consequently happen that the orientation of the molecules on the top face is different to the corresponding orientation on the face below. The angle between them is  $\alpha$ , let us say. It then appears that there is a gradual transition from one orientation to the other on the way through; the substance assumes a helicoidal or twisted arrangement. If a polariser is set parallel to the molecules on the lower surface, the analyser, in order to obtain extinction, must be set, not in the perpendicular direction but at an angle  $\alpha$  thereto. We have a straightforward example of the twisted medium which we have already considered. Both ordinary and extraordinary rays follow the screw-like arrangement of the structure, the vibration in the one remaining always normal to the molecule, and therefore to the optic axis, while the other vibration is always parallel to it. In this case there is no deflection of the extraordinary ray.

The substance in the nematic state does not always assume the simple arrangement in plane sheets, in which the axes are parallel to the surface. If it is cooled quickly from the amorphous phase, or if less care is taken in the preparation of the glass plates, it becomes full of complicated vortices

and intertwinings. Among these are the fine lines or threads from which the phase derives its name ; they are especially obvious where the preparation is thick. The threads are lines of discontinuity giving rise to optical effects, in accordance with the calculations made above. A thread might be a line which is the meeting place of crystal axes at all points of its length, as in the smectic case. There is now no necessity, however, for the line to be part of an ellipse or hyperbola because it has no companion, with which to form a pair of focal conics. Or again it might be a line round which the medium is circulating, corresponding to a vortex ring, which is either complete or anchored at two ends. The molecules and the optic axes are then tangential to circles having the line as axis. Sometimes a line marks the boundary between two portions in which the axial directions are different.

In these cases, the ordinary ray is not deflected as it passes by the thread, unless it passes very close to it. There must then be a deflection of the ordinary ray because the thread is visible. It may be that there is actually a hollow cylinder—perhaps vacuum—providing a reflecting surface ; or it may be that the excessive strain of the medium close to the thread actually alters the refractive index of the ordinary ray. The latter explanation would involve the introduction of a principle not used hitherto in these considerations. It has been sufficient, so far, to ascribe the optical effects to geometrical arrangement.

The extraordinary ray, on the other hand, may be deflected, since it passes through a region in which the crystal axis is continuously changing its direction in the plane containing axis and ray.

From this point of view we see at once the explanation of a very remarkable and characteristic appearance of the nematic substances, which is illustrated in the photographs of Plate III. These are photographs of the same preparation, taken one after the other as quickly as possible so as to avoid changes due to the continuous movement of the liquid. The light entering from below is not polarised but passes through an analyser after crossing the preparation. The obvious difference between the two photographs is due to the fact that the analyser was rotated through about  $90^\circ$  between the two exposures. The threads that look narrow and clear in one photograph are distorted in the other; a close comparison will show that otherwise the two photographs are identical. The remarkable feature which demands explanation is the fact that all the threads in one part of the picture should be clear simultaneously, while in another part they are all blurred. We remember, however, that there can be a skin or pellicle, to use Friedel's term, in contact with the glass surface; in other words the previous existence of a solid crystal there has left molecules on the glass which all point the same way, like a flock of birds on the ground which all head up into the wind. This sets the orientation of other molecules in the near neighbourhood of the glass, and though the molecules may be orientated in all kinds of ways between the top and the bottom of the preparation, the change is never discontinuous except in the "thread" itself; even then the continuity passes round the thread, if not through it. Consequently the ordinary rays emerge with their vibrations perpendicular to the axis of the pellicle at the point of

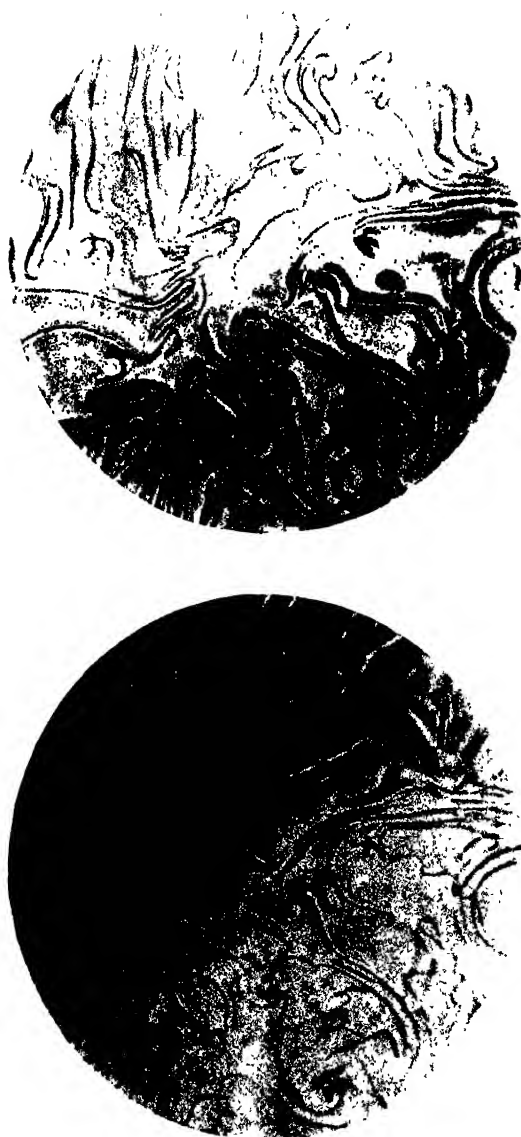


PLATE III.—The two photographs show the same substance, para-azoxyphenetole in the nematic phase, at two moments separated by as short an interval as possible. The only difference is that the position of the analyser in the one case is approximately at right angles to its position in the other. No polariser. The clearer portion of each photograph is seen by ordinary rays; and the other by extraordinary rays.

emergence ; though when the rays passed by the thread the vibrations were all parallel or perpendicular to the thread, according to the view which we take of the nature of the thread. The vibrations of the extraordinary rays are all perpendicular to those of the ordinary. The analysing Nicol can therefore be set so as to extinguish all the extraordinary rays and transmit only the ordinary, so that the threads are seen clearly. And if the Nicol is set so that the view is obtained by means of the extraordinary rays, the images are blurred because those rays are deflected out of their course by going near the threads. The whole effect depends on the compelling power of the pellicle, setting an arrangement at the surface to which the internal arrangement, whatever it may be at a distance from the surface, must gradually conform as the distance from the surface diminishes. The vibrations have been orientated in a different direction at each point of the tortuous thread, but have all been pulled into one direction when they emerge. In the illustration there are two regions ; in one of them the molecular direction in the surface happens to be more or less at right angles to the direction in the other : so that when one part, seen by ordinary rays, is clear, the other, seen by extraordinary rays, is confused. The optical effects of nematic threads have been studied by H. Zocher and his colleagues.\*

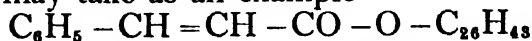
When the para-azoxyanisole is cooling down from the liquid the first appearance of a change of phase is the formation of separate groups of molecules, which between crossed Nicols give the effect illustrated in Plate IV. Each group shows, besides

\* Zocher u. Birstein—Zeit. f. phys. Chemie, A. CXLII, p. 113, 1929.

finer details, a cross, the arms of which are parallel to the principal planes of the Nicols. A similar effect may be observed in certain solids such as strontium carbonate or salicin, and occasionally lavas and glasses, and in organic substances such as cholesteryl acetate. It is an indication that in each group there is a nuclear point from which the axes of minute crystals radiate uniformly in all directions. In two of those directions, mutually at right angles, the axes of the crystals are parallel respectively to the principal planes of the crossed Nicols. If the preparation is rotated with respect to the Nicols, the cross does not move. The group is therefore independent of any pellicles; it is floating freely in the middle of isotropic liquid. The molecules either radiate from the nucleus in the centre, or are arranged along concentric circles as if there were a vortex. Either arrangement gives the cross. On one side of the illustration, the groups are coalescing and are attaching themselves to the glass above and below. The connections are irregular but there are traces of the original simple arrangements of the groups. On the border between the liquid crystal phase are larger groups formed by the coalescence of smaller groups.

The third class of liquid crystals has been termed by Friedel the cholesteric. In some ways its properties resemble those of the smectic and nematic classes. But we meet here with a new effect, a brilliant coloration of which the causes and laws have never been fully explained.

We may take as an example



Cholesteryl cinnamate.

Solid -  $156^\circ$  - cholesteric  $197^\circ$  - liquid.

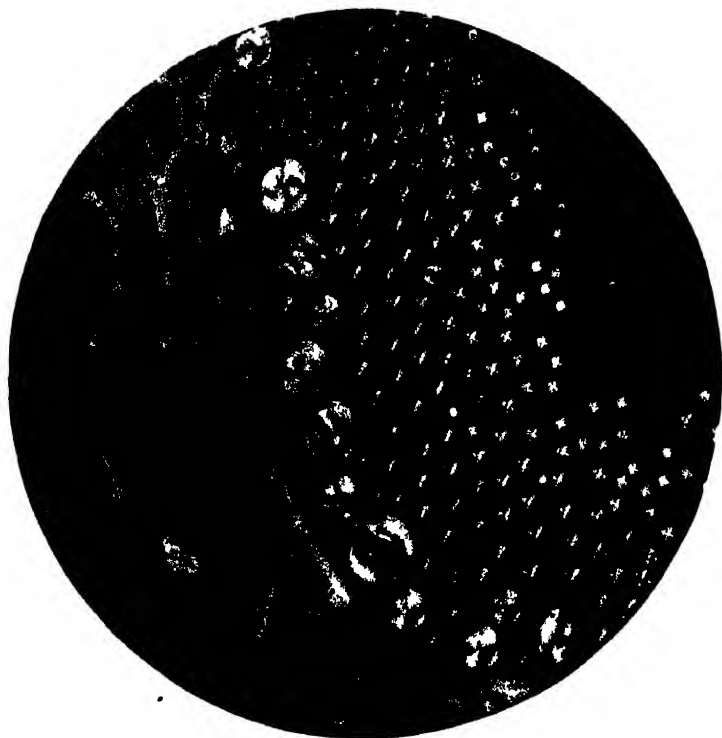


PLATE IV — Para-azoxyanisole cooling, between crossed Nicols. On the left the nematic state is advancing. Small drops are forming in the liquid on the right. The arms of the crosses are parallel to the principal planes of the Nicols. The larger drops are formed by coalescence of the smaller.



When this substance is allowed to cool down from the liquid phase it presents at first a confused appearance of a focal conic structure. But a slight mechanical disturbance causes it to assume a form in which it reflects brilliant colours like those of a peacock's feather. The colour depends on the temperature, being vivid green at the higher temperatures and golden-bronze at the lower. But the most remarkable effect is that the reflected or, more correctly speaking, scattered light is circularly polarised. If the incident light is circularly polarised, it is reflected if the circulation is represented by a right-handed screw, and transmitted if the screw is left-handed. In the case of some other cholesteric substances this is reversed. More remarkable still is the fact that the scattered light is right-handed, like the absorbed light to which it is due. In all other known cases of the reflection of circularly polarised light the sense of the rotation is reversed. Let a circularly polarised ray be allowed to fall upon the preparation, the rotation being of that sense which leads to scattering, and let the scattered light be viewed through a Nicol and a quarter-wave plate. It is then curious to observe that when the scattered light is made to disappear by suitable adjustment of the receiving system, any light reflected from ordinary substances such as the brass frame on which the slide rests, is at its best and *vice versa*.

These substances, when in their characteristic state, are optically active to an extraordinary degree, represented sometimes by as much as a whole turn in the hundredth of a millimetre. The activity depends on the wave length in a curious way. It is very large on either side of the wave

length which is the most intensely scattered : at that wave-length itself it cannot be determined. It falls away at increasing distances on either side of that wave length, and is in the opposite sense on the two sides. The whole effect is suggestive of resonance and anomalous dispersion, from which point of view it has been discussed by various writers without definite conclusion.

In a thin layer the cholesteric substance presents a marked appearance of stratification ; the effect is known by the name of Grandjean's planes. The circular polarisation of the scattered light and the length of its wave seem to be closely associated with the optical activity and the stratification.

This short account of the chief properties of "liquid crystals" is very far from complete. Nothing has been said of the influence of electrical and magnetic fields on molecular arrangement, which is strong in the case of substances in the nematic phase but absent in the smectic, except during the process of cooling from the liquid. Nor has reference been made to the peculiar facility with which the molecules of liquid crystals dispose themselves in particular directions on fresh cleavage faces of solid crystals. Nor have the viscosity effects been described. In spite of these omissions the account may help as an introduction to the extensive literature of the subject, the more so because the accumulated observations are scattered over many scientific journals, and because also the various workers are far from agreement as to their interpretations.

[W. H. B.]

## APPENDIX

# I

*The path of the extraordinary ray in a plane in which the crystal axis at any point is directed towards a fixed point in the plane.*

In Fig. 10 the ellipse drawn in full line is the velocity ellipse of the extraordinary ray for the medium below  $T_0T$ , and  $T_0T$  is the axial direction at  $C$  in that medium. The wave front  $T_0P_0$  is advancing in the direction  $P_0C$ : and if the medium

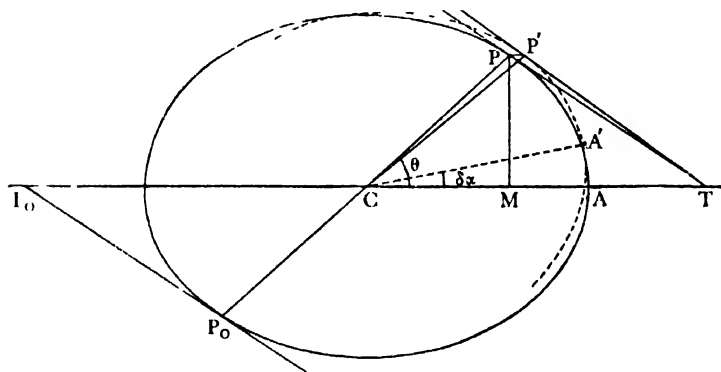


FIG. 10.

above  $T_0T$  were the same as below, the wave would continue to advance in the direction  $CP$  and would eventually reach  $TP$ . But if, on crossing the boundary  $T_0T$ , there is a slight change  $\delta\alpha$  in the direction of the crystalline axis, so that the velocity ellipse now takes the form shown in dotted line, the new direction of the ray is  $CP'$ , and the wave front is eventually  $TP'$ .

It can be readily shown that  $PP'$  is parallel to  $T_0T$  and is equal to  $\delta\alpha \text{ PM } c^2/b^2$  where  $c$  and  $b$  have their usual meanings. The semi-axes of the

ellipse are  $a$  and  $b$ ;  $c^2 = a^2 - b^2$ . The change in the direction of the ray on crossing the line  $T_0T = PCP' = PP' \sin \theta / CP = \delta a \cdot \sin^2 \theta \cdot c^2 / b^2$

where  $\theta$  is the angle between the ray and the axial direction at C. The change in the angle between the ray and the axis =

$$\delta \theta = -\delta a (1 + \sin^2 \theta \cdot c^2 / b^2)$$

the negative sign being given to the change because in the figure the angle between  $CP'$  and the new axis is less than that between  $CP$  and  $CT$ . The integration of this equation gives

$$\tan(na + \text{const}) = -n \tan \theta, \text{ where } n = a/b.$$

The path of the ray can be expressed in polar co-ordinates,  $r$  and  $\alpha$  (Fig. 5), in which case  $\tan \theta = r d\alpha / dr$ .

A second integration with suitable choice of constants gives

$r \cos n\alpha = k$ , where  $k = OA$  in Fig. 5, which is Grandjean's result.

## II

*The passage of polarised light through a helicoidal sheet, the ray being normal to the sheet.*

Suppose that the strata forming the sheet are parallel to the  $(xy)$  plane, and that the ray is directed along the axis of  $z$ .

In each stratum there are two principal directions mutually at right angles. Suppose that the effective specific inductive capacities in those directions are  $K_1$  and  $K_2$ , and let the former make an angle  $\alpha z$  with the axis of  $x$ .

We enquire whether it is possible for the ray to consist of an elliptic vibration of constant ellipticity, the axes of which in each stratum are parallel to the two principal directions; and if so, on what conditions?

The electric forces at any point may be written

$$a \cos \omega \left( t - \frac{z \sqrt{K}}{c} \right) : b \sin \omega \left( t - \frac{z \sqrt{K}}{c} \right)$$

where  $\omega = 2\pi \times$  frequency,  $c$  is the velocity of light in space, and  $c/\sqrt{K}$  the velocity in the medium.

The electric inductions along the elliptic axes are respectively

$$K_1 a \cos \omega \left( t - \frac{z \sqrt{K}}{c} \right) : K_2 b \sin \omega \left( t - \frac{z \sqrt{K}}{c} \right)$$

where  $K_1$  and  $K_2$  are specific inductive capacities.

The electric forces ( $E_x$  and  $E_y$ ) and electric inductions ( $D_x$  and  $D_y$ ) along the axes of co-ordinates are therefore

$$E_x = a \cos \omega \left( t - z \sqrt{K}/c \right) \cos az - b \sin \omega \left( t - z \sqrt{K}/c \right) \sin az$$

$$E_y = a \cos \omega \left( t - z \sqrt{K}/c \right) \sin az + b \sin \omega \left( t - z \sqrt{K}/c \right) \cos az$$

$$D_x = K_1 a \cos \omega \left( t - z \sqrt{K}/c \right) \cos az - K_2 b \sin \omega \left( t - z \sqrt{K}/c \right) \sin az$$

$$D_y = K_1 a \cos \omega \left( t - z \sqrt{K}/c \right) \sin az + K_2 b \sin \omega \left( t - z \sqrt{K}/c \right) \cos az$$

Maxwell's equations for a plane wave travelling parallel to the axes of  $z$  require that

$$\frac{\partial E_x}{\partial x} = \frac{1}{c} \cdot \frac{\partial B_y}{\partial t} = \frac{1}{c} \cdot \frac{\partial H_y}{\partial t}$$

where  $B_y$ , the magnetic induction along  $y$  is equal to  $H_y$ , the magnetic force along  $y$  because the permeability is practically unity.

$$\text{Also } \frac{\partial H_y}{\partial z} = \frac{1}{c} \cdot \frac{\partial D_x}{\partial t}$$

$$\text{so that } \frac{1}{c^2} \cdot \frac{\partial^2 D_x}{\partial t^2} = \frac{1}{c} \cdot \frac{\partial^2 H_y}{\partial x \cdot \partial t} = \frac{\partial^2 E_x}{\partial z^2}$$

$$\text{similarly } \frac{1}{c^2} \cdot \frac{\partial^2 D_y}{\partial t^2} = \frac{\partial^2 E_y}{\partial z^2}$$

but this equation need not be used as it gives the same result as the other.

If now we substitute the values for  $D_1$  and  $E_1$  we find that if the equations are to be true for all values of  $z$  and  $t$  we must have

$$\sqrt{K} - \frac{ac}{\omega} = \sqrt{\left(\frac{K_1 a + K_2 b}{a + b}\right)} \text{ and } \sqrt{K} + \frac{ac}{\omega} = \sqrt{\left(\frac{K_1 a - K_2 b}{a - b}\right)}$$

We thus have two equations to find  $a/b$ , the ellipticity, and  $K$  which gives us the velocity  $c/\sqrt{K}$ . If we put  $a=0$ , thus annulling the twist, the equations are satisfied if  $K=K_1$  and  $b/a=0$ , or  $K=K_2$  and  $a/b=0$ ; which is the ordinary solution for a crystal.

The term  $ac/\omega = \lambda \sqrt{K}/p$  where  $\lambda$  is the wave length in the medium and  $p$  is the pitch of the screw. This follows from the facts that  $a=2\pi/p$ , and  $\omega/\sqrt{K}=2\pi/\lambda$ .



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